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MARCH 1959

THE 1957 EXPLOSIVE ERUPTION ON IWO JIMA, VOLCANO ISLANDS*

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ABSTRACT. An explosive eruption occurred without warning on March 28, 1957, near the center of Iwo Jima, a small volcanic island midway between Guam and Tokyo, Japan. The eruption of steam, volcanic sand, and volcanic sandstone and conglomerate blocks began suddenly at 11:55 A.M. local time, continued for 65 minutes, and ended abruptly. Coarse ejecta were thrown as high as 150 feet; dust and steam rose to heights of 200 to 300 feet. No juvenile material was ejected. An elliptical crater 90 to 110 feet in diameter and 45 feet deep resulted. Deposits were concentrated to the western (lee) side where they ranged in thickness from 22 feet near the crater to less than one inch 300 feet to the west. About 50 minutes after the eruption a second crater formed by collapse 75 feet northwest of the eruption crater. The circular collapse crater was 115 feet in diameter and 55 feet deep. Many ground cracks and small faults with displacements up to 8 inches were formed nearby during and following the eruption. Steam and other gases issued from the craters, faults, and cracks following the eruption, and some sublimates were deposited. No significant change of fumarolic activity was noted on other parts of the island before, during, or after the eruption.

The eruption resulted from the sudden release of an underground accumulation of steam under high pressure beneath artificial fill adjacent to an abandoned airfield. The eruption does not seem to indicate an increase in volcanic activity on Iwo Jima.

INTRODUCTION

An explosive eruption occurred March 28, 1957, on Iwo Jima (Sulfur Island), a small volcanic island south of Japan that acquired fame during World War II. The writers arrived on the island the following day to investigate the eruption and make a five-day geologic reconnaissance for the U. S. Air Force which maintains an emergency landing field on the island.

Iwo Jima lies between 141° 17¼′ and 141° 20¾′ E Longitude and 24° 44¾′ and 24° 49′ N Latitude. It is about 5 miles long, as much as 2½ miles across, has an area of approximately 8 square miles, and is the largest of the group of three islands forming the Volcano Islands (Kazan-rettō). The island's shape is roughly triangular and has been compared with that of a pork chop.

The highest elevation, 525 feet, is on Suribachi-yama, a volcanic cone at the southern tip of the island. A low isthmus, called Todorigahara, joins Suribachi-yama to the larger northern portion of the island. The northern portion of the island, called Motoyama, is a nearly flat plateau with a maximum elevation of about 375 feet near the present airstrip. Near the center of the plateau is a small area of very active solfatara, the Motoyama solfatara.

Suribachi-yama and Motoyama have rocky and cliffed shorelines with a few short sand and boulder beaches. The Todorigahara isthmus is bounded by two long, straight volcanic sand beaches.

* Publication authorized by Director, U. S. Geological Survey.

At present the island has no native inhabitants. However, prior to World War II it was occupied by Japanese who mined sulfur and grew a few crops, including sugar cane. The island has no harbors or other port facilities. Supplies for the island are brought by air or by shallow-draft ship which can land supplies on either of the two long volcanic sand beaches flanking the isthmus.

ACKNOWLEDGMENTS

The writers appreciate the excellent cooperation of U. S. Air Force personnel on Iwo Jima, especially Lt. Col. Frank McCormick and Chaplain Parker. The eye-witness account of Lt. James D. Sirockman and his extensive knowledge of the island's geography were invaluable. The keen observations of Airman Emon Clark and his substantiating photographs were an outstanding contribution.

GEOLOGIC SETTING

The Volcano Islands including Iwo Jima, Kita Iwo Jima, 42 miles to the north, and Minami Iwo Jima, 38 miles to the south, are situated on the crest of one of the prominent submarine ridges forming the east boundary of the Philippine Sea. A fourth island, 3 miles northeast of Minami Iwo Jima, was formed by volcanic eruptions in 1904 and again in 1914; both times it was destroyed by marine erosion (Wakimizu, 1920). At intervals its position is marked by agitated and discolored water over the submarine vent.

Iwo Jima is composed almost entirely of lava flows, pyroclastic rocks, and volcanic sediments (fig. 1). Northern Iwo Jima consists chiefly of a thick sequence of well-jointed, poorly stratified tuff, named the Motoyama Bluff tuff by Tsuya (1936, p. 458). The lower part of the formation is unconsolidated to poorly consolidated grayish coarse tuff, lapilli tuff, and tuff breccia. Fragments include abundant pumice and obsidian, less abundant trachyandesite and siliceous sinter, and scarce syenite. In places along the northeast coast an unconformity separates the lower and upper parts of the formation. The upper part is a yellowish gray succession of fine pumiceous tuff with interbedded layers of coarse tuff. Bedding, which is fairly well developed at some horizons in the upper part, generally dips outward at angles of 8-10 degrees from the active solfataric area near the center of Motoyama. The origin of the tuff is uncertain. Tsuya (1936, p. 459) considers it to be a submarine deposit that has been domed by a later intrusion.

Trachyandesite lavas which are partly intrusive into the lower part of the Motoyama Bluff tuff are exposed at scattered localities along the northeast coast. Small intrusive masses of trachyandesite are also exposed on the upper surface of the northeast part of the Plateau (Tsuya, 1936, p. 462; Swenson, 1948, p. 998). At the inner edge of terraces along the north coast, flow lines in the trachyandesite are nearly vertical or fan outward; along the shore, they are nearly horizontal or dip gently to the northeast. Columnar jointing is conspicuous in several exposures. In general, the trachyandesite represents a single eruption that probably was submarine. The petrography of the lava has been described by Tsuya (1936, p. 476) and MacDonald (1948, p. 1011).

On the south end of Motoyama, the Motoyama Bluff tuff is overlain by a

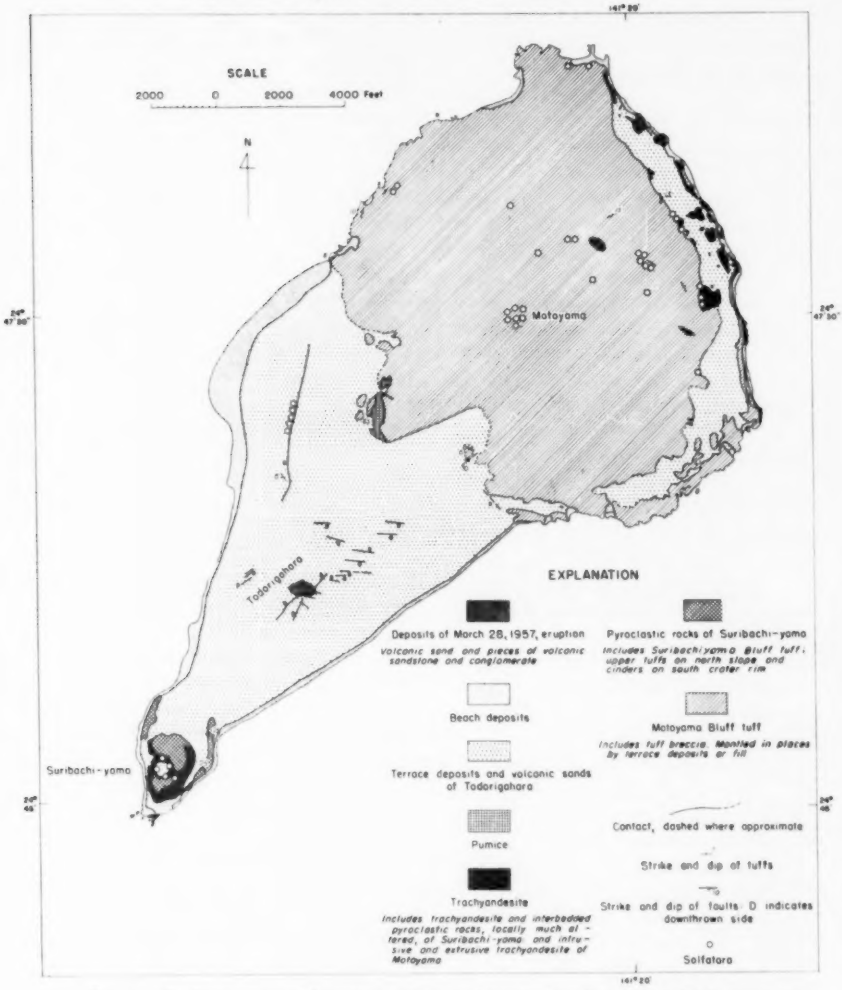
SCALE
2000 0 2000 4000 Feet
N
Motoyama
Suribachi-yama
Toderigahara
EXPLANATION
Deposits of March 28, 1957, eruption
Volcanic sand and pieces of volcanic sandstone and conglomerate
Pyroclastic rocks of Suribachi-yama
Includes Suribachi-yama Bluff tuff; upper tuffs on north slope and cinders on south crater rim
Beach deposits
Motoyama Bluff tuff
Includes tuff breccia, bedded in places by terrace deposits or fill
Terrace deposits and volcanic sands of Todorigahara
Contact, dashed where approximate
Pumice
Strike and dip of tuffs
Trachyandesite
Includes trachyandesite and interbedded pyroclastic rocks, locally much altered, of Suribachi-yama and intrusive and extrusive trachyandesite of Motoyama
Strike and dip of faults. D indicates downthrown side
Solfatara

Fig. 1. Geologic map of Iwo Jima, Volcano Islands, based on 5-day field reconnaissance by the writers, photo interpretation, and maps by Tsuya (1936) and Swenson (1948).

deposit of bedded pumice up to 30 feet thick. The pumice is easily eroded, and deep gulleys have formed where the surface vegetation or other protection has been disrupted. The pumice is probably a partly reworked subaerial deposit.

A small area of raised, Recent reef limestone has been reported at the northeast edge of Motoyama (Swenson, 1948, p. 999) and elsewhere on the upper surface of Motoyama (Toyoshima, 1932, p. 530). These localities were not visited by the writers.

Terraces which are covered by beach deposits, alluvial material, and wind-blown sand are well developed on the west, northeast, and east sides of Motoyama. All appear to be Recent (Homma, 1925).

The isthmus, Todorigahara, is composed almost entirely of bedded, poorly consolidated, volcanic sands and gravels derived mostly from erosion of pyroclastic rocks at the north or south ends of the island. The sands and gravels are moderately to well sorted and consist chiefly of fragments of trachyandesite glass. Locally the deposits have been cemented or altered by groundwater and solfataric activity. At depth they are probably underlain by the Motoyama Bluff tuff.

Suribachi-yama is a small volcanic cone that is now dormant. A thick succession of poorly stratified coarse tuffs, lapilli tuffs, and tuff breccias form the base of the cone (Tsuya, 1936, p. 460). These deposits are called the Suribachi-yama Bluff tuff and resemble parts of the Motoyama Bluff tuff. Fragments of obsidian, some of which differ from those in tuffs at the north end of the island, are very common in the Suribachi-yama Bluff tuff.

The cone itself is comprised of trachyandesite lavas, sills and the Suribachi-yama Bluff tuffs. Much of the material has been highly altered by fumarolic action, especially within the crater of the cone. The south rim of the cone has a thick irregular deposit of dark red cinders and scoria; the north rim and north slope have a mantle of well-bedded tuffs resembling the basal Suribachi-yama Bluff tuff.

Faults, both active and inactive, are numerous on the island. At the south edge of the northern plateau numerous faults were noted in the Motoyama Bluff tuff. Some of these extend into the overlying pumice, some do not. Along the west coast an active fault, marked by a low scarp and numerous fumaroles, requires constant maintenance of roads which cross it. This fault is apparently the same as one described by Krauskopf (1948, p. 210). Many post-1945 fault scarps ranging from less than an inch to nearly 3 feet high interrupt the paved surface of an abandoned airfield on Todorigahara.

Active solfataras are present at many places. The largest and most active areas are near the center of Motoyama, along the northeast coast, and in the crater of Suribachi-yama. Scattered smaller areas exist at many places on Motoyama, along the west coast, and in the vicinity of the March 28 eruption on Todorigahara. In the Motoyama solfataric area, there are several boiling mud pots in which temperatures of as much as 102°C have been recorded in vapor jets (Tsuya, 1936, p. 469). A ground-temperature survey made in 1923 by Toyoshima (1932) indicated several areas having near-surface temperatures near 100°C. Sulfur is being deposited in small quantities around some larger solfataras and locally was mined commercially by the Japanese.

DESCRIPTION OF THE ERUPTION

An eruption of steam, sand, and blocks of sandstone and conglomerate began without warning at 11:55 A.M. on March 28, 1957, on Todorigahara, about 1.3 miles northeast of Suribachi-yama (pl. 1). The eruption continued for approximately 65 minutes and then ended abruptly. Dust and steam rose to heights of 200 to 300 feet and coarse material was ejected as high as 150

PLATE 1

Photograph (by Airman Emon Clark, U. S. Air Force) of March 28, 1957 eruption. View to southwest along abandoned runway. Suribachi-yama is in the background.

feet. Some hissing and roaring sounds were heard but in general the eruption was not particularly noisy. The material was ejected from a single crater (pl. 2A); a second crater to the northwest was formed by collapse about 50 minutes after the end of the eruption (pl. 2B). Following the collapse all activity ceased except some minor emission of steam from small nearby fissures and ravelling of loose sediments on the walls of the two depressions.

At the time of the eruption, winds were from the east at 7 to 9 miles per hour, sea-level pressure was 1016.7 mbs and the temperature was 70°F. These atmospheric conditions and those preceding the eruption were generally normal for spring. Rainfall during the preceding three months was only slightly below normal. A heavy rain fell during the late evening of the 28th following the eruption.

On the day after the eruption, small amounts of gas and steam were issuing from the base of the explosion crater and from fissures to the east. No activity was noted in the collapse crater except minor ravelling and slump of material as drying took place. On March 31, emission of gases increased, and clouds of steam and irritating gases filled the explosion crater. Although mostly clear of visible gases, heat waves and acid fumes, probably HCl, were observed in the collapse crater. Three dead birds, one of which was seen to die from inhaling noxious fumes, were noted in the crater.

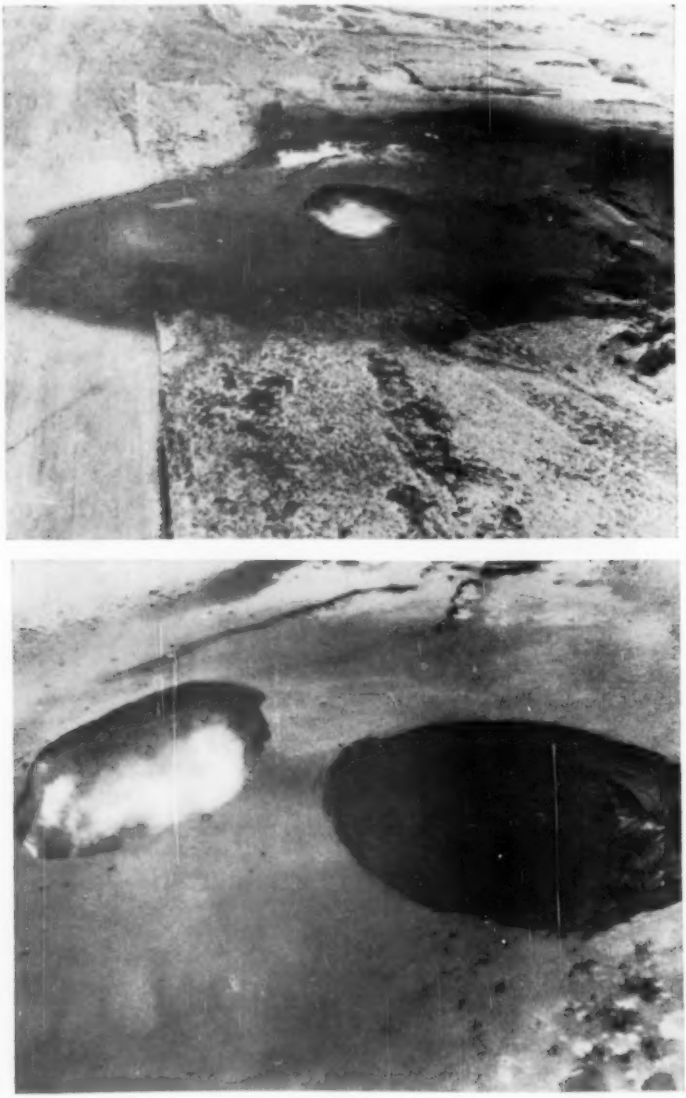

PLATE 2

Aerial oblique photographs of the craters formed on March 28, 1957. (Photos by Airman Emon Clark, U. S. Air Force)

Above. View to southwest of explosion crater about 50 minutes after the eruption.

Below. View to south showing the explosion crater and the collapse crater in the process of formation about 55 minutes after the eruption.

Emission of steam and gases continued from both craters and from fissures near the craters from March 31 through the end of observations on April 2. The amount of steam expelled decreased from a maximum during the morning of March 31 to practically none on April 2. By April 2 a very thin layer of sublimates had been deposited on surfaces adjacent to some larger fissures.

CRATERS

The craters which resulted from the eruption are located on Todorigahara in an area of artificial fill adjacent to and near the south end of an abandoned runway (pl. 2 and fig. 2). Elevation of the site before the eruption was about 205 feet. On March 29th the explosion crater had a maximum diameter of 105 feet, a minimum diameter of 90 feet, and a depth of about 45 feet from the

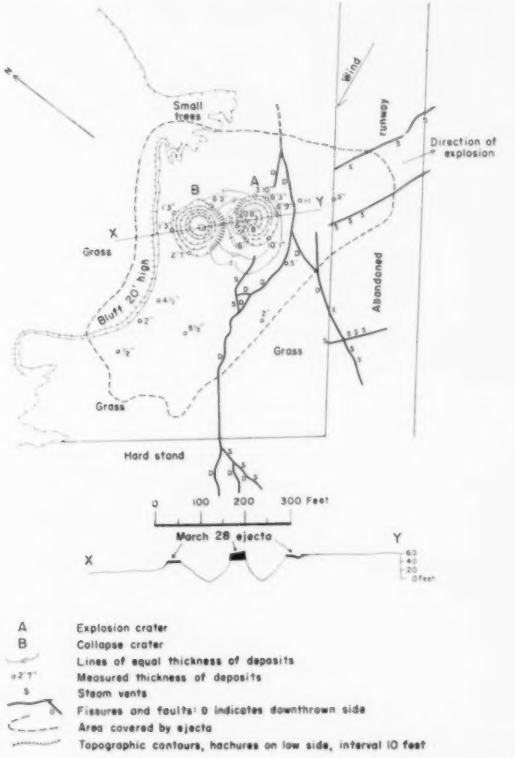

Fig. 2. Pace and compass map of craters and deposits of March 28, 1957, eruption. A thin discontinuous deposit of ejecta extends west of the area of general continuous cover outlined on the map. The southwest end of the low fault scarp (up to 3 feet high) trending northeast through the center of the map was probably formed before the eruption, but some new movement was associated with the eruption especially in the vicinity of the craters.

lowest point on the crater rim and 40 feet from the former ground level. At the time of the eruption, the crater appeared to be about 30 to 50 feet across. Upper parts of the crater wall were vertical (pl. 3A); the lower portion had the shape of an inverted cone, partly because of slumped material. Below the former ground surface, the walls appeared to be chiefly poorly consolidated, well-bedded volcanic sands and gravels; a few small ledges of cemented sands were visible.

The center of the collapse crater was about 110 feet west of the center of the explosion crater. It was nearly circular with a measured mean diameter of 115 feet and depth of 55 feet below the lowest part of the rim and 52 feet below the old ground surface. The ground near the edge of the crater was broken by concentric slump cracks. Below the old ground surface the interior had the shape of an inverted cone, the lower two-thirds of which was comprised of slumped volcanic sands. Walls formed in the newly ejected material were vertical, with some overhanging ledges supported by grass and other vegetation on which the deposits lie.

DEPOSITS

Most solid ejecta from the explosion crater ranged in size from fine silt to coarse sand and was concentrated on the western, leeward side. Large blocks, forming a very small proportion of the deposits, were almost entirely on the east and southeast sides of the crater; none were found in deposits to the west. The largest blocks were near the east rim of the crater and were more than 3 feet across. Blocks up to a foot across were scattered over the abandoned runway more than 150 feet from the rim (pl. 3B).

The maximum measured thickness of the deposits was 22 feet near the west rim of the explosion crater. From this maximum the deposits thinned westward to about 2 feet at a distance of 100 feet, 1 foot at 150 feet, and about one inch at 300 feet (fig. 2). Further west a thick mat of grass made measurements unreliable. To the east the deposits thinned from 5 feet at the crater rim to about 2 inches at a distance of 50 feet and were absent at 300 feet. Estimated total volume of the ejected solid materials is 10,000 cubic yards.

The ejected material is comprised chiefly of porous to dense trachyandesite glass. Larger blocks included poorly consolidated tuff and volcanic sands, a small amount of cemented pumiceous tuff, and a few fragments of lava. Some larger blocks with iron cemented layers are unlike any material exposed in the walls of the craters. All of the material was apparently derived from the explosion crater or at some depth beneath it; none was juvenile.

Distribution of the larger fragments reflects an eastwardly directed component of the explosion and distribution of the finer particles the direction of the prevailing winds at the time of the eruption. Both conditions are evident in photos of the eruption (pl. 1).

FAULTS AND FISSURES

Numerous small faults and fissures exist in the vicinity of the new craters and are especially evident on paved surfaces of the abandoned runway and

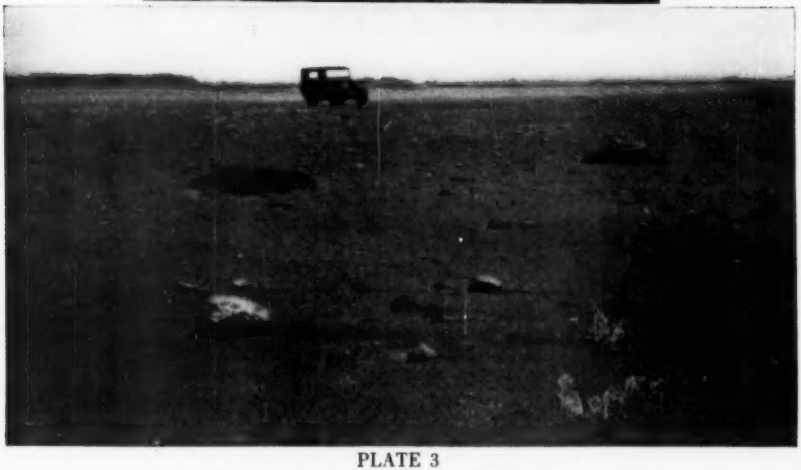

PLATE 3

Deposits of ejecta from the explosion crater.

Above. North wall of explosion crater showing thick deposits of ejecta. Note the dark band and buried vegetation indicating the former ground surface.

Below. Coarse ejecta on surface of abandoned runway. View east.

adjoining hardstands. Some of the faults observed to the east, west, and south of the eruption crater appeared to be new breaks formed during or soon after the eruption; displacement along one of these faults amounted to 8 inches within 5 days (March 29 to April 2, 1957). Most of the faults and fissures, however, predate the eruption, for grass and other vegetation grows in the cracks and on low scarps. A few older cracks may have been reactivated by the eruptive activity. Whether the formation of fresh breaks and renewed activity took place before, during, or soon after the eruption was not determined.

Steam and other gases were issuing from most fresh breaks and several older ones. At some places, white sublimates were being deposited from the gases. East of the runway, similar sublimates from older fissures have formed crusts on the surface up to 1/16th inch thick.

Most fractures and faults observed on the surface of the abandoned runway trend approximately east-west or slightly east of north (fig. 1). An en echelon arrangement is suggested by offsets along some fractures. Faults on the southern half of the strip are downthrown on the north; those on the northern half are downthrown on the south side.

No evidence for new activity along faults was found at distances of more than 1,500 feet from the eruption center nor was there any definite indication of changes in the rates of older continuing activity on faults and in solfataras on other parts of the island. Some recent movement of the active fault along the west coast may be related to the eruption.

VEGETATION AND ANIMAL LIFE

Grass and brush within 300 feet of the explosion crater was considerably damaged by burial beneath the erupted materials and by fumes emitted along fissures and faults (pl. 3B). The odor of decaying vegetation remained strong during the period of investigation. Numerous dead field mice and birds were seen on or partly buried in the deposits of the eruption.

CAUSE OF THE ERUPTION

The eruption resulted from the sudden release of a subsurface accumulation of steam under high pressure. Reasons for the accumulation of steam in the generally loose deposits and sudden release of the accumulation are unknown, but the eruption may be related to redistribution of heat flow as suggested by Toyoshima (1932, p. 534) for a similar phreatic explosion which occurred near the west coast in July 1922.

The oblique eastward component of ejection suggests that the highest subterranean pressures were west of the explosion center. Expulsion of steam and other materials from this area presumably left a void that was later filled by material from the collapsed crater.

Homma (1925) and others have suggested an actively rising magma to explain the rapid uplift, numerous active faults, and thermal phenomena on Iwo Jima. Well-developed terraces of Recent age at elevations of 150 feet and more surround much of the island. Evidence for historic uplift during the past century is cited by Homma (1925) and others; and this is substantiated by

several shoreline features observed by the writers, including rapidly expanding beaches on the west side of the island and elevated positions of fumaroles and other features which were reported to have been at or near sea level prior to 1920. Post-1945 movement along faults, indicated by offsets in the pavements of roads along the west coast and the abandoned airfield on Todorigahara, ranges up to 3 feet. There is little evidence for changes in overall solfataric activity or ground temperatures. However, comparison of the map published by Toyoshima in 1932 with plotted positions of presently known areas of high ground temperature suggests some redistribution of heat and maximum heat flow (see also Toyoshima, 1932, p. 531). In 1955 a sudden rise in the temperature of the floor and cold water supply in one of the Air Force billets, now named the Iwo Onsen (hot spring), furnished striking proof of local redistribution of heat flow (C. G. Johnson, personal communication).

Geophysical studies that include gravity, seismic, and ground temperature surveys and extended observations of tilt, leveling, tides, and other phenomena are needed to determine whether a moving magma exists at depth or if there are other causes for the rapid changes which are taking place on the island.

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EXPERIMENTAL ABRASION
3. FLUVIATILE ACTION ON SAND

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ABSTRACT. Former experiments by the author dealt with pebble sizes down to 1 cm. The present investigation extends to sizes of 0.4 mm. The mechanism was again that of a current in a circular channel of concrete, but additional tests were made in revolving cylinders. Limestone, feldspar, and mainly quartz were used.

In these sizes mechanical abrasion is found to be entirely negligible in river transport. The elimination of limestone and feldspar during fluviatile transport is therefore not a result of mechanical action. Down-current variation in roundness must be attributed to shape-sorting and/or chemical attack, or to addition from new sources.

INTRODUCTION

A number of authors have experimented on the mechanical abrasion of sand grains (e.g. Galloway, 1919; Anderson, 1926; Thiel, 1940; Berthois and Portier, 1957). Following Daubrée, they have all used the technique of revolving horizontal cylinders. Unfortunately this is a very poor imitation of what happens in a river, as the present writer has pointed out in earlier papers (Kuenen, 1958). The exaggerated abrasion by this method has led these writers to overestimate the effectiveness of fluviatile action.

Nor have attempts at shape analysis, of samples taken at various points along river courses, given entirely satisfactory results. Shape sorting obviously has an influence, but its efficiency is not known (Russell and Taylor, 1937).

Since so little trustworthy information is available on the rate of abrasion in fluviatile transportation, the present writer has adopted a different experimental technique which he believes to be superior.

In two earlier papers (Kuenen, 1955; 1956) results were reported of experimental fluviatile abrasion of pebbles between 6 and 1 cm in diameter, rolled by a current. The most useful results were obtained by using cubes, so that the influence of shape was invariable and the effect of size, composition, and bed roughness could be studied separately and quantitatively assessed. But other shapes were also experimented with. In the present investigation sizes from 1 cm downwards were to be studied. However, before experiments on the abrasion of sand and small pebbles during fluviatile transportation can be undertaken it is necessary to understand the mechanism by which the grains are carried forward in nature.

TRANSPORT OF GRAINS ON A RIVER BED

Three theoretical possibilities can be imagined: (1) transport in suspension, (2) a bed load moved by bottom traction (rolling and jumping), grains moving separately, (3) mass movement by which a layer on the bottom is pushed forward bodily, presumably with diminishing velocity from the surface to a depth of perhaps a few centimeters.

Suspension.—It is obvious that grains carried in suspension are hardly at all attacked mechanically, because they move parallel to their neighbors and almost at the same velocity. Besides, they move so swiftly that the entire river course is covered in a short time. Experimental imitation of such transport for abrasion measurements therefore appears unnecessary.

Bottom traction.—This is without doubt an important process. Wherever

ripple mark is formed the load has been transported as separate grains which come to rest when deposited in the lee of a ripple crest. Likewise, lamination of a current deposit is a sure proof that the material has undergone grain by grain sorting on the bottom before coming to rest.

Sandy river deposits normally show lamination throughout: in part horizontal, in part with fore-set structures, and in part as current ripple lamination or mega-ripple lamination. There can be little doubt, therefore, that in a braiding or meandering river bottom traction is the chief mechanism of sand transportation. Hence an experimental investigation should include this type of transport.

Mass movement.—This mechanism is usually not considered for rivers (Twenhofel, 1945; Sundborg, 1956), but as the writer has observed it in experimental turbidity currents, it is important to decide whether it perhaps plays a part in fluviatile transport also. Experiments on sand abrasion have been carried out, as noted above, by placing a fairly large quantity of sand and water in a revolving cylinder. The resulting movement does not appear to have been analyzed by these authors. It depends strongly on the amount of sediment in the cylinder and on the relative amount of water (see Kuenen, 1958). But it probably does simulate the kind of transport called mass movement here.

However, a number of independent arguments can be raised against the suggestion that such a mass movement would play a part in river transport:

1. This kind of movement could not produce any but the coarsest lamination, because no sorting of grains is involved and there is bound to occur a thorough mixing in the moving layer. The laminated structure of river deposits therefore argues against mass transport. But it must be admitted that such transport should be restricted to deeper river channels and therefore it can not be represented in the usual kind of deposits, which have been formed beside or on the margin of channels.

2. In laboratory tests of river transport a mass movement is never observed. But it is conceivable that this is due to too small a scale.

3. The lamination and sorting observed in the deposits of tidal flat channels is incompatible with mass movement.

4. In experimental turbidity currents with a sandy load, mass transport can actually be observed. However, it is the result of excessively swift deposition from a heavily loaded current. Already during the deposition a strong compaction to half the original thickness is seen to take place in a minute or two. As the water between the grains escapes and allows them to come into contact the mass movement comes to an end. The deposits of natural turbidity currents show that, with declining velocity, bottom traction sets in and laminated deposits form, then rippling takes place and finally smooth lamination is again produced. Mass movement is therefore the result of abnormal mobility under conditions lacking in a river. At most it might play a small part if a spate in a small stream dies out swiftly.

5. If the grains on the bed of a river are separated by a film of water there can be no grinding action. If they are in contact the friction between the grains must prevent mass movement because it exceeds frictional drag by the overlying water.

6. The amount of sand carried by the Rhine across the German-Dutch border averages 250,000 m^3 per year, or 8 liters per second. As the breadth of the river bed between groins is 300 meters, the transport averages roughly one gram per second per centimeter width.

With an estimated bottom velocity of 50 cm/sec and grain velocity of 25 cm/sec the average thickness of the moving layer of sediment works out at 0.2 mm, or considerably less than the median particle diameter. As part of this load moves by saltation, it is evident that the remainder on the bottom must be rolled as separately moving grains. In other words, even in a groined channel and with an abundance of sand available, a comparatively swiftly flowing river like the Rhine transports so little sand that mass movement cannot be active. Admittedly transportation is much greater during periods of flood, but as an increase of the suspended load takes care of much of this excess the amounts moved along the bottom are still much too small for any mass movement to be involved.

Together these arguments show convincingly that all or practically all transport along a river bed is by traction. Hence experiments on abrasion should concentrate on grain by grain movement.

EXPERIMENTAL TECHNIQUES

In the present investigation the same methods were used as formerly with pebbles. This time the circular moat was coated with concrete made of coarse, rather angular sand. A rotating four-armed paddle driven electrically was used

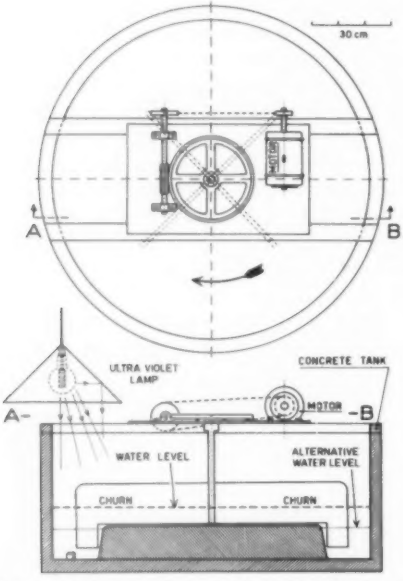

Fig. 1. Apparatus used for experimental fluviatile abrasion of small pebbles and sand sizes.

for producing the current (fig. 1). Cubes, crushed minerals and natural sand grains were tested. The advantage of studying cubes is not only that the variations due to shape are eliminated, but also that the percentage of loss can be judged fairly accurately by the relative degree of rounding (pl. 1d).

At first, the decision to use cubes caused difficulties because it was found impossible to shape them accurately smaller than 4 mm. Moreover, large numbers were now required for a reliable determination of loss in weight. Finally a satisfactory method was developed. A rectangle the size of a match box was first cut and carefully shaped. This was mounted on a machine tool and one or two dozen parallel grooves were cut with a circular dentist's diamond saw (diameter 22 mm) (fig. 2). The spacing was chosen so as to leave walls of the required thickness. Then the grooves were filled with hard Canada balsam and new slots were cut at right angles to them so as to leave pillars of the right size. After filling again, the surface was ground true and a stout piece of glass was mounted on top. A thin slice was sawed off next to the glass and ground to the desired thickness. Then by dissolving the balsam a few hundred to a thousand cubes of the right size were set free. In quartz the smallest size that could thus be produced was 0.6 mm, because of difficulties with chipping in such brittle material. But from lithographic limestone Mr. Ludemann, technician, succeeded in turning out 1200 cubes of 0.4 mm in two day's work (pl. 1e).

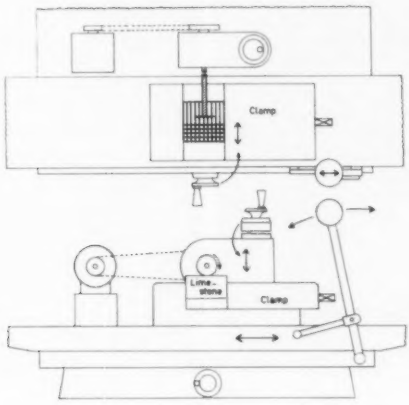

Fig. 2. Machine tool used for cutting small cubes.

The second technical difficulty was how to measure rolling velocities. As the distance of transport has to be determined from time and velocity, the latter is an important datum. It is of course out of the question to follow a grain of a millimeter diameter rolling on the bottom of a swift churning current. Covering a grain with luminescent paint was found to be a satisfactory method. Then with a shaded ultra-violet lamp playing on one side of the moat one can watch the radiating particle shoot past on the opposite dark side. The only drawback is that the layer of paint slightly alters the shape of a small

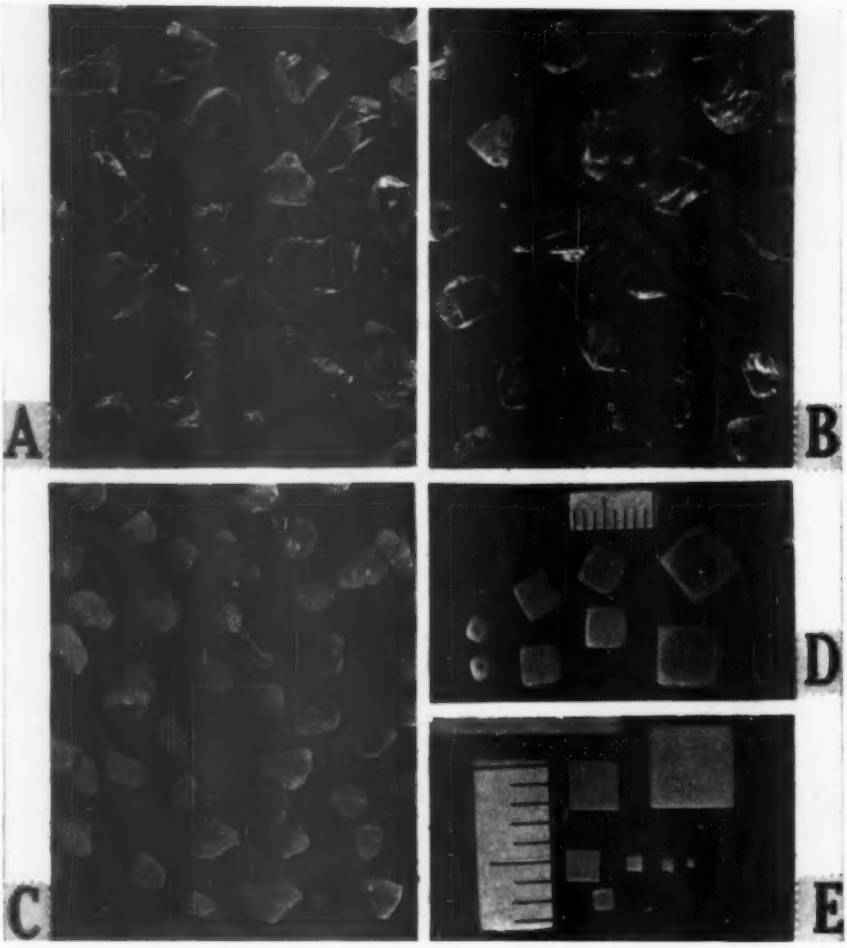

PLATE 1

a = crushed quartz 1.5-2 mm.

b = the same after 248 km fluviatile transportation on concrete floor at 47 cm/sec; loss 0.96%.

c = quartz from weathered granite 1.2-1.5 mm, after 425 km fluviatile transportation at 46 cm/sec; loss 0.52%.

d = cubes of lithographic limestone. From left to right: two cubes of 2.5 mm abraded in wind tunnel on concrete over 64 km, wind 13.5 m per second, grain velocity 2 to 3 m per second, loss 24%; two cubes of 4 mm, fluviatile transport 16 km on concrete at 26 cm per second, loss 3.2%; two cubes of 4 mm, fluviatile transport 16 km on concrete at 171 cm per second, loss 4.9%; two cubes of 6 mm, fluviatile transport 16 km on concrete at 141 cm per second, loss 4.7%.

e = cubes of limestone 10, 6, 4, 2.5, 1.6, 0.8, 0.6, 0.4 mm, the 1 mm cube is of quartz. The scale is in millimeters.

particle. The velocity of the 0.4 cubes was therefore ascertained by extrapolation from that of larger cubes, rather than by measurement.

A third difficulty is to measure the loss in weight of such small objects. By using 100 cubes at a time and weighing on a microbalance reasonable accuracy could in most cases be attained. But still herein lies doubtless the largest source of error, apart from occasional losses of cubes.

Several experiments were repeated more than once and mostly the outcome showed losses of the same order of magnitude. For instance in experiment 438 use was made of 100 quartz grains of river sand, 1.2-1.5 mm in diameter travelling at 45 cm per sec. The three weighings before and after 112, 119, and 120 kilometers of travel were as follows:

773.523 mg	.475	.417	.342
.531	.477	.419	.354
.535	.487	.430	.350

The per kilometer losses are 0.000057, 0.000063, 0.000078 percent, averaging 0.000067. However, in some experiments unaccountable failures occurred, such as apparent increase in weight or abnormally high losses.

As the tests with quartz had to be continued for days or even weeks to obtain measurable losses, it was not possible to repeat all of them. It will become clear presently that no great accuracy is required, as even the greatest losses are insignificant anyhow.

After each test the material was recovered by inserting a deep net of wire gauze that fitted the bottom of the moat. The grains were washed in by the current and it seldom took more than a few minutes to catch all of them. Occasionally one or two small grains managed to elude catching for a long time. It also happened that some were washed onto the central platform. Therefore the water level was lowered so that no grains could escape from the moat (fig. 1).

In some respects the conditions in the experiment are unnatural. In the first place the bottom is formed of hard concrete instead of loose sand. In the second place the grains were never taken into suspension, not even the smallest size at travelling velocity of 84 cm per second. Even very little saltation takes place, probably because of the smooth bottom and the absence of loose impactees. Both factors should tend to exaggerate the loss. On the other hand, loss in the experiments is roughly halved because each grain is only impactor and not also impactee. It will be assumed, as in the former experiments, that these opposing influences cancel each other out. But in nature so much transport of sand is in suspension that the abrasion deduced from the present experiments is almost certainly too great.

The technique of a revolving cylinder will be dealt with later. First the results obtained in the moat will be discussed separately for the various kinds of material used.

SOLNHOFEN LIMESTONE

First, limestone cubes of 20, 15, 10, 6, 4, and 2.5 mm were tested, mainly

Solnhofen lithographic limestone[1]. The abrasion losses over the first 16 km and at various rolling velocities are shown in figures 3 and 4. In the latter a few results obtained in former experiments on a pebbly floor are added.

It is obvious that when the cubes are rolled on a bottom of much finer grain the influence of velocity is complex but not very significant. On a pebbly floor of comparable or larger grain size the abrasion is greater and it increases much more with velocity. Size also has only a moderate influence in the case of small pebbles rolling on a "sandy" floor, especially at high velocities. This is also apparent from figure 5.

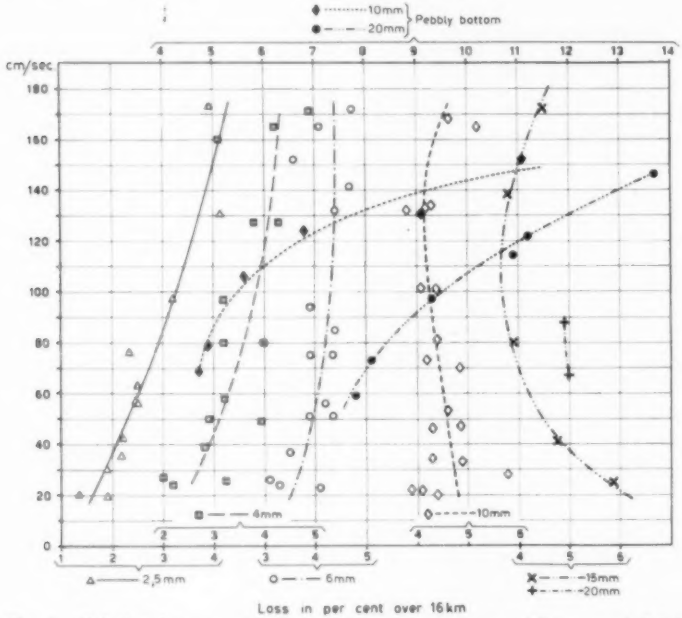

Fig. 3. Relation between velocity and loss in percent per kilometer of Solnhofen lithographic limestone cubes of small pebble sizes when rolling on a concrete floor. Distance of travel 16 km. Some results added for cubes rolling on a pebbly floor. This figure is mainly for showing how the lines are drawn through the scattered points. Figure 4 gives an overall picture.

The curious inversion of the influence of velocity for the 15 mm cubes is noteworthy. The reason is probably that they can only just be kept in motion at low speeds. Normally pebbles travel by revolving round a horizontal axis without vertical movement of their centre of gravity. But at the lower limit of movement they are seen to wobble along and frequently fall sideways onto a face, thereby turning around a vertical axis for a moment. This should cause a grinding movement and accounts for the extra abrasion. This conclusion is

[1] Values obtained from an oolitic limestone were reduced by 3/11 because then the average corresponded with that of the lithographic limestone.

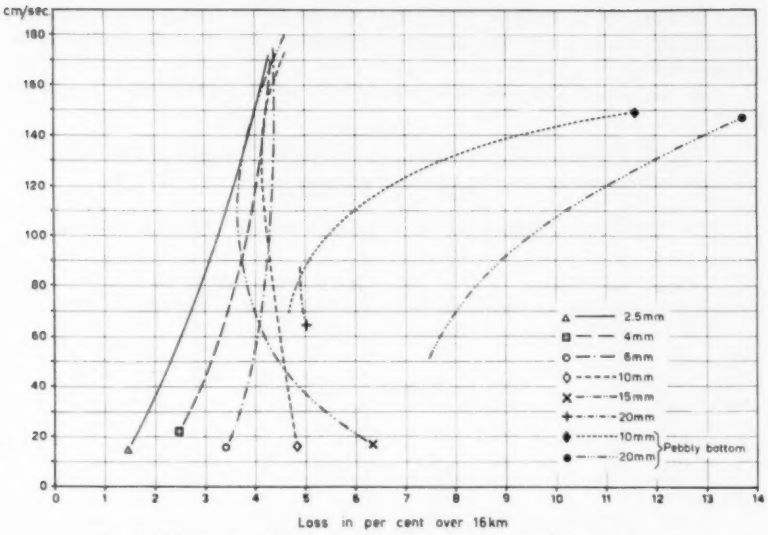

Fig. 4. The lines of figure 3 combined in their true relative positions.

confirmed by the fact that on the faces of cubes that had wobbled along slowly the demarcation between intact and abraded surfaces was less sharply drawn. For smaller grains the floor is too rough and the velocity used too high for this type of movement.

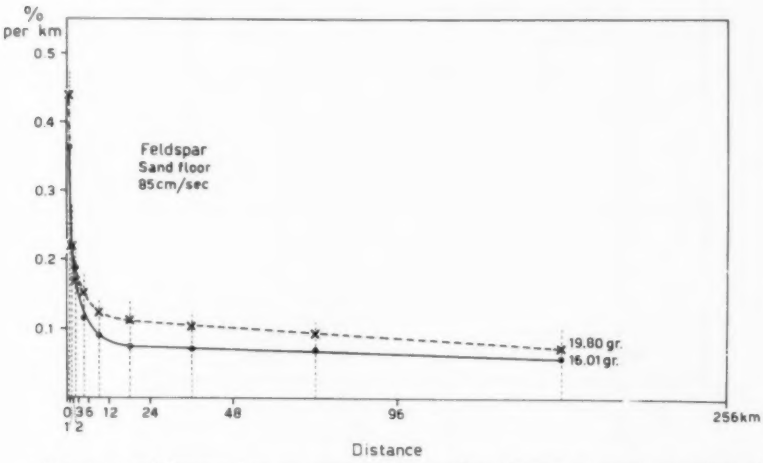

Fig. 5. Per-kilometer loss on concrete floor against distance of travel for cubes of white oolitic limestone (W.L.) and of Solnhofen lithographic limestone (Lith.L.). Chipping has evidently stopped after about 2 km of travel.

Contrary to what might be expected smaller cubes show a greater influence of velocity. This is a strong argument against transport in suspension in the experiments.

It was found that—as with pebble sizes on a pebbly floor—increasing

TABLE 1

Loss in 1/100 Percent per Kilometer Suffered by Cubes of Limestone Rolling under Water

L = lithographic limestone, W = white limestone. Small pebble sizes

Rock	Veloc. cm/sec	Size mm	Number	Distance of travel in km								
				0-¼	¼-½	½-1	1-2	2-4	4-8	8-16	16-32	32-64
W	67	20	1	47	60	67	41	43	39	35		
W	81	10	3	20	47	42	40	36	33	33		
W	85	6	4	66	42	37	29	35	31	35		
L	101	10	1	60	26	32	24	23	22	22	18	
L	101	10	1	57	19	32	24	23	22	22		
L	101	10	1	43	33	32	28	23	21	22		
L	101	10	1	40	40	28	24	22	22	22		
L	101	10	1	50	31	29	24	23	21	22		
L	97	25	10	124	93	23	19	14	15	15	12	13

TABLE 2

Loss in 1/100 Percent per Kilometer Suffered by Cubes of Lithographic Limestone Rolling Under Water. Small Pebble Sizes

Veloc. cm/sec	Size mm	Number	Distance of travel in km		
			0-16	16-32	32-64
35	—	—	13.5	11.8	10.2
20	2.5	10	8.4	8.0	7.9
57	—	—	15.5	12.5	10.8
76	—	—	14.5	13.7	12.1
130	—	—	25.9		
173	—	—	24.6		
26	4	5	20.2		
49	—	—	24.5		
165	—	—	36.1		
23	6	3	25.6		
51	—	—	27.2		
75	—	—	27.2		
141	—	—	29.4		
172	—	—	29.6		

roundness reduces the loss per kilometer (fig. 5). Again, this decrease of abrasion is most marked in the beginning. At first the sharp edges chip, but after 2 km this process has come to an end and the decrease in loss per kilometer becomes quite small.

In most respects the smallest pebbles (2.5 mm) rolling on a coarse sand floor are comparable to larger cubes rolling on a pebbly bottom. However, the

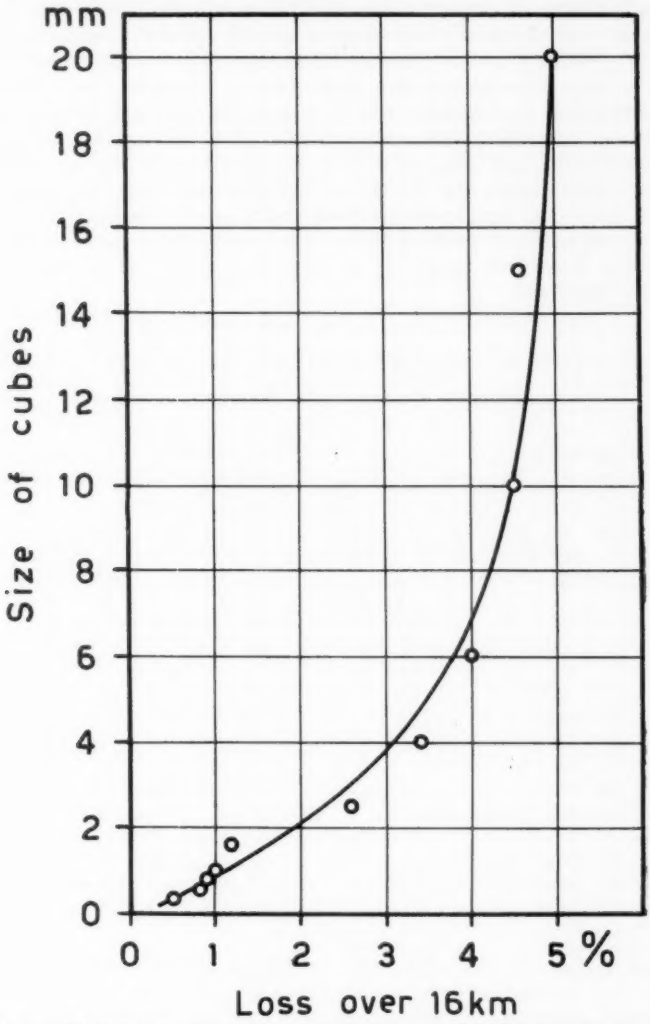

Fig. 6. Relation between size and loss over the first 16 kilometers on concrete of lithographic limestone cubes, Averaged for various velocities.

smaller scale does not result in identical laws of abrasion because the nature of the rock remains the same instead of showing a related reduction in strength. As a result the gentler impacts do not lead to cracking and the loss at high velocities remains moderate (see analysis of abrading process in former paper, Kuenen, 1956, p. 350-352).

Smaller sizes down to 0.4 mm were also tested, sizes that are comparable to the grains fixed in the concrete. The loss over a given distance is found to decrease with size in the same manner as with pebbles on a pebbly bottom (fig. 6). Whether there is a lower limit in size beyond which abrasion falls to zero, as many investigators have suggested (see Twenhofel, 1945), could not be ascertained. It is probable that in nature fine sand grains travel only in suspension, and then no abrasion will take place. The problem is, after all, academic at this stage, because with decreasing diameter the loss of sand-sized grains drops to values that can have no significance in nature long before there is any question of the abrasion perhaps becoming zero. However, it is possible that a combination of chemical and mechanical abrasion is significant and then a possible lower limit in particle size that can undergo bottom traction could become important.

TABLE 3

Loss in 1/100 Percent per Kilometer Suffered by Cubes of Lithographic Limestone Rolling Under Water. Sand Sizes

Veloc. cm/sec	Size mm	Number	Distance of travel in km										
			0-2	2-16	0-16	16-32	0-32	32-64	16-64	64-128	32-128	0-128	±120-±200
19	1.6	40	10.0	6.8		7.9							
21	1	120	1.2	8.4		1.0				0.7			
76	1	25			4.0	2.7		2.4					
40	1	25			4.4	2.7		2.2					
20	1	25			4.5	3.1		2.9					
61	1	25			4.0	4.0		2.0					
36	1	50			3.6								
64	1	50			4.4								
170	1	38			14.5								
123	1	38			11.2								
21	0.8	100	48.4	2.3					0.8	1.6			
39	0.8	100			4.1	0.5				0.9			
57	0.8	100					7.6	1.7		1.7			
78	0.8	100			6.2	3.1		2.2		1.9			
20	0.6	120	13.8	2.7						0.3			
83	0.6	100			5.8				2.5				
56	0.6	100					2.8				0.8		
83	0.4	100										2.7	neg.
84	0.4	100			2.8	2.8		0.0		0.0			
42	0.4	100			2.3	1.3		0.0					
56	0.6	80											0.6
84	0.4	94											0.3
86	1.6	40								5.4			

How slight the loss from small grains is can be illustrated by the finding that on the stretch from 240 to 360 km distance, at a velocity of 84 cm per second, the abrasion of limestone cubes of 0.4 mm is only 0.003 percent per kilometer.

The influence of size and decreasing angularity is brought out distinctly in figure 7. It should be realized that a difference in shape due to loss of one percent in weight cannot be detected by eye except for the first dulling of corners (see plate 1a and b). The losses in the lower rectangle when continued over more than 50 km transport produce 1 percent of abrasion or less.

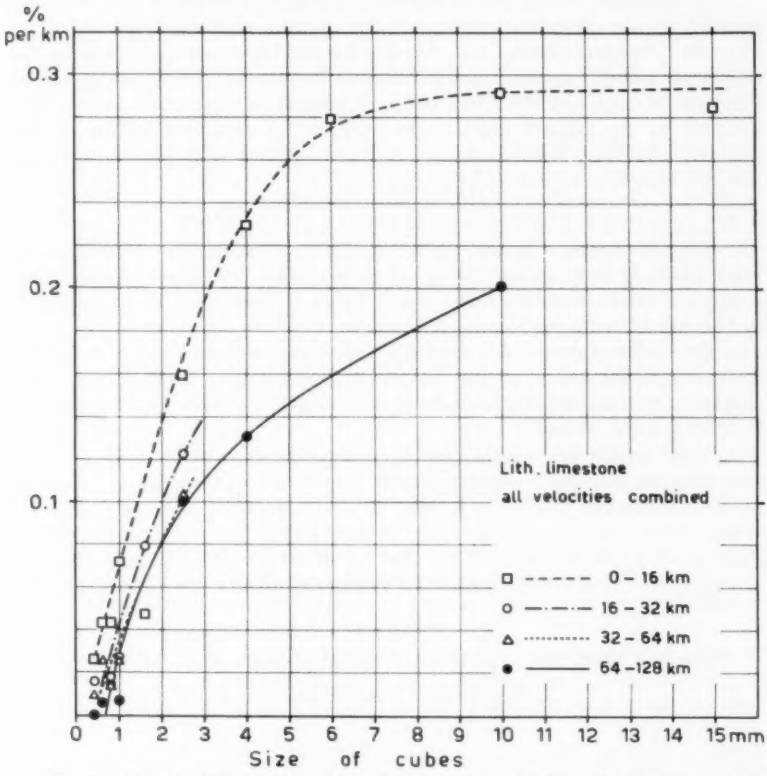

Fig. 7. Relation between size and per-kilometer loss of lithographic limestone cubes on concrete floor. Data for consecutive stretches of travel shown separately. All velocities are combined.

MIXED GRAIN SIZES

An important question is whether the addition of a large quantity of coarser or of finer sand will change the rate of abrasion significantly. Experiments on this problem were made with lithographic limestone cubes. First 80 cubes of 0.6 mm were tested at 55 cm per second and showed a loss of 0.006

percent per km. Then 1200 times their number of angular quartz grains of 1.2-1.5 mm were added. The velocity had to be increased to 78 cm to keep the cubes from being buried under a heap of sand. The abrasion loss changed to 0.008 percent per km. From other measurements it follows that this increase is fully accounted for by the higher velocity. Hence, the abrasion is not increased by the presence of a dominant load of much larger grains.

A test on cubes of 0.4 mm was not quite satisfactory because out of 94 cubes one was lost in a kilogram of quartz grains of 1-1.2 mm. But it was shown at least that no significant increase in abrasion had occurred.

In the same manner, it was demonstrated that the addition of a dominant quantity of fine sand to a few large grains causes a noticeable decrease of the abrasion. The per-kilometer loss of fourty 1.6 mm limestone cubes travelling at 84 cm per second dropped from 0.054 to 0.019 percent by the addition of one kilogram of sand of 0.4-0.6 mm and at a velocity of 59 cm per second. This decrease to one third is much more than can be explained by the smaller velocity. The same result had already been obtained with pebbles, that are abraded less when sand is added.

QUARTZ

A series of tests on quartz cubes was also undertaken. They were found to react similarly to limestone grains but to lose much less. Some characteristic results are shown in tables 4 and 5 and figure 8. The values for quartz are 5 to 40 times as low as for Solnhofen limestone.

The surface velocity of a natural stream is two to three times greater than the speed of the grains on the bottom. A grain velocity of 40-50 cm/sec is equivalent to transport in a normal major river and 90-100 cm/sec corresponds to a fairly swift stream.

Doubt can be felt whether the abrasion of cubes is of the same order of magnitude as of natural angular grains. Therefore tests were made on quartz from a weathered granite soil (pl. 1c). Interpolation between measured values shows that quartz cubes of 1.5 mm would lose somewhat less than 0.001 percent per km after about 200 km of travel. The amount of 0.0014 measured on the granite quartz of 1.2-1.5 mm is in very good agreement, be-

TABLE 4

Loss in 1/100 Percent per Kilometer Suffered by Cubes of Quartz Rolling Under Water. Sand Sizes

Veloc. cm/sec	Size mm	Number	Distance of travel in km					
			0-16	16-32	32-64	64-128	128-256	370-730
35	2.5	2	0.8	0.4	0.2	0.2	0.1	
130	2.5	2	4.0	2.3	1.5	1.7	1.2	
40	1.0	60	0.6	0.0	0.2	0.07	0.05	
123	1.0	60	1.9	—	0.7			
31	0.6	50	—	—	0.041	0.037		
78	0.6	50	—	0.55	0.31	0.09	0.06	0.03

TABLE 5

Fluviatile Abrasion of Cubes of Lithographic Limestone and Quartz, Grains from Granite, Subangular River Sand, and Crushed Quartz

Size mm		Velocity cm/sec	Distance in km	Loss in % limestone	Loss in % quartz	Loss in % per km km	limestone	quartz
cubes	2.5	130	32		0.98	16-32		0.023
			256		4.16	128-256		0.012
	2.5	35	32	4.05	0.13	16-32	0.118	0.004
			256		0.47	128-256		0.001
	1.5	86	96	5.7		32-96	0.054	
	1	40	64	1.85	0.17	32-64	0.022	0.002
			192		0.24	128-192		0.0005
	0.6	31	128		0.150	64-128		0.0003
	0.4	84	368			248-368	0.0027	
1.2-1.5 granite		46	32		0.18	8-24		0.0024
			264		0.51	32-332		0.0014
1.2-1.5 granite		113				264-454		0.0024
		46				454-573		0.0013
1.5-2 river sand		94	152		0.26			0.0017
1.5-2 river sand		42	222					0.0002
1.2-1.5 river sand		45	350					0.00007
1.5-2.0 crushed crystals		114				312-492		0.0036
		47				492-610		0.0003

cause some feldspar and mica adhered to the quartz grains and the loss must therefore be higher than from pure quartz.

Finally, angular chips from crushed quartz crystals were tested. These grains are extremely fragile and sharply angular. The per kilometer loss is distinctly larger than of cubes or granite grains of the same size travelling at the same rate. However, it is still a very small value.

The influence of velocity is shown on granite quartz by the result of doubling the speed which causes twice the loss per kilometer. It falls back to almost the original amount when the velocity is brought back to the original value.

In various tests with other material the speed tended to have a larger influence.

A test was made on 1.5-2 mm grains from a river sand showing roundness of .4 according to Krumbein's classification (1941). At a high speed of travel (94 cm per second) the loss was 0.0017 percent per km, but at 42 cm per second it was only 0.0002 percent per km. Even less abrasion was found for subangular river sand of 1.2-1.5 mm. For medium, subangular quartz grains the per kilometer loss should be roughly 0.00005 percent.

To realize how very slight this abrasion is, it should be noted that 20.000

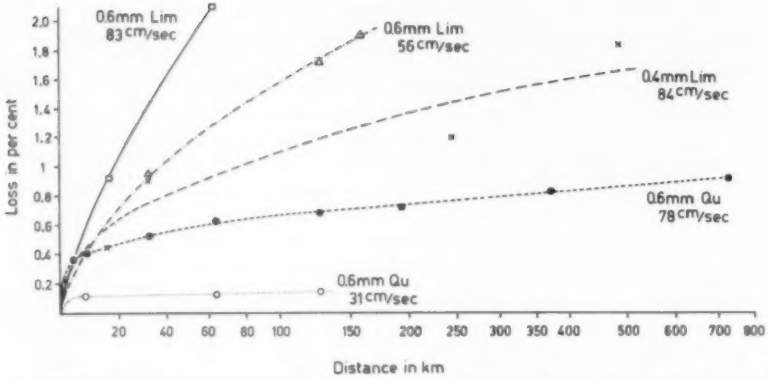

Fig. 8. Relation between total loss and distance of travel for sand size cubes of lithographic limestone and quartz, travelling at various velocities on concrete floor.

km of transport would cause no more than 1 percent loss, an amount that, as already remarked, would be very difficult to detect on an angular grain and quite invisible on a subangular one. In a cycle of denudation the average distance of transport by rivers is less than 1000 kilometers. Consequently the mechanical fluviatile abrasion of medium sand grains during twenty cycles would cause less than 1 percent loss in weight, and after the first one no further rounding would be detectable.

In former experiments (Kuenen, 1956, fig. 19) it was found that pieces of irregular shape must, on the average, lose 20 percent in weight to become well rounded (Cailleux roundness 400 = .7 to .8 Krumbein). For one-half mm quartz grains this would require more than 400,000 km of rolling, because the loss must be even less than 0.00005 percent per km after the grains have become subrounded.

FELDSPAR

A specimen of pegmatite orthoclase was crushed and sieved. From these fractions grains of a more or less compact shape were selected. These were rolled a few hours in a bottle with sand, to remove flakes on the point of chipping off. With this material the results shown in table 6 were obtained in the concrete channel.

This shows that, as with quartz, decrease in size, in velocity and in angularity cause a decrease in abrasion. The abrasion is about twice that of quartz under similar conditions, a difference that is much smaller than might be expected. After the initial dulling of the edges feldspar of sand size must be transported several thousands of kilometers to become visibly more rounded by abrasion. This tallies with observations on natural river sands as made by Russell (1937) and Koldewijn (1955).

In petrographic investigations of sands the presence of feldspar, and especially of angular grains of this mineral, is very commonly taken as a trustworthy indication of proximity to the source. This inference may be correct in

TABLE 6

Abrasion Losses of Orthoclase Fragments

grain size 1.5-2 mm, velocity 94 cm/sec	
0- 60 km	0.0152 percent per kilometer
60-190 km	0.0037 percent per kilometer
190-350 km	0.0042 percent per kilometer
grain size 1.0-1.2 mm, velocity 90 cm/sec	
0- 50 km	0.0062 percent per kilometer
50-190 km	0.0084 percent per kilometer
190-350 km	0.0008 percent per kilometer
350-560 km	0.0010 percent per kilometer
grain size 1.0-1.2 mm, velocity 37 cm/sec	
0- 60 km	0.0039 percent per kilometer
60-190 km	0.0013 percent per kilometer
350-510 km	0.0004 percent per kilometer

most cases, but the argument that feldspar is too soft and too easily cleaved to stand up against river abrasion, is not confirmed by the present results. Chemical weathering, while the grains await further transport in sand bars and flood plains, must be held almost entirely responsible for any elimination of feldspar during transport that can be deduced from change in composition of a river load.

An additional experiment was carried out with two larger pieces of the

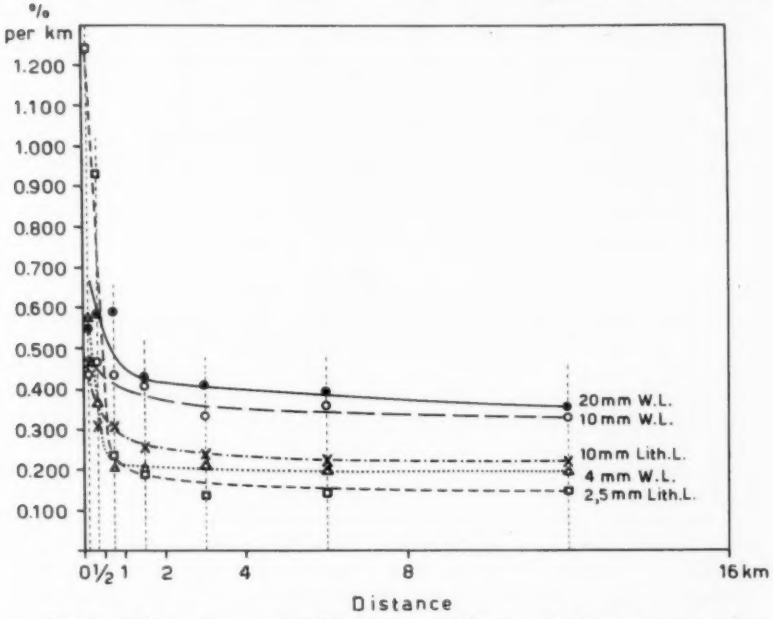

Fig. 9. Relation between per-kilometer loss and distance of rolling on concrete floor for two fragments of orthoclase feldspar.

same feldspar (fig. 9). For these comparatively large pieces rolling on a fine-grained floor the chipping continues for about 20 km. Afterwards the loss becomes again quite small, about 0.1 percent per kilometer.

Revolving cylinder tests

The latest experiments on the rounding of sand in a revolving cylinder, in this case made of concrete, are those by Berthois and Portier (1957). They obtained about 10 times the loss found in the present investigation for the same material tested in the circular moat. Their result is 50 or more times the loss deduced for medium subangular sand. The reasons for this difference are (1) the use of crushed quartz crystals, which are more fragile and angular than natural grains, (2) the unnaturally violent attack sustained in a rolling, rough-walled cylinder, (3) a different definition of the term "loss". In an earlier

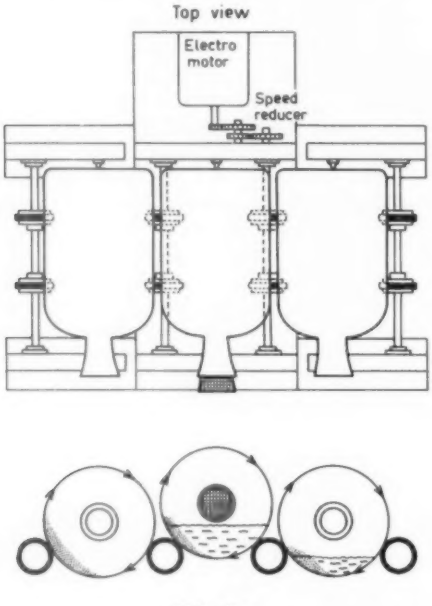

Fig. 10. Apparatus used for testing abrasion of sand samples in revolving glass bottles.

paper (Kuenen, 1958) reasons have been given for preferring the method of a current and of defining "loss" so as to coincide with "abrasion".

But the technique of a rotating cylinder has the advantage that if a glass bottle is used the influence of chemicals added to the water can be examined (fig. 10). In one test 100 grains of subangular river sand 1.2-1.5 mm were added to 500 gr of river sand 0.2-0.3 mm and 1 liter of tap water. The velocity of the inner wall of the bottle was 46 cm per second. The average loss of the test grains over a distance of 1000 km was 0.00009 percent per kilometer. The

loss of the same grains and sand in 1/10 n. acetic acid over 600 km (tested in the middle of the other run) was 0.00011 percent per kilometer. The difference is less than the marginal error. In other words no significant influence is produced by the acid.

An experiment with $NaHCO_3$ failed because after 522 km one of the test grains was lost. But the weight of the remaining ones showed that at any rate no abnormally high abrasion had occurred.

The reason why the loss is so extremely small is that the wall of the glass bottle is polished and remains so. The grains slide smoothly along the bottle wall, and do not roll nearly as "far" as the distance covered by the wall. To a considerable extent the grains do revolve over and against each other but their mutual abrasion is evidently extremely slight.

Conclusions

These experiments show that the mechanical fluviatile abrasion of small pebbles is slight and that it becomes extremely slow for quartz grains of less than 2 mm diameter. Several writers have been led to a similar conclusion (e.g. Twenhofel, 1945), but the present tests show that mechanical fluviatile abrasion is even less than they imagined. For subangular course-grained sand it is less than 0.1 percent per 1000 km of transport. For smoothly rounded medium sand it may be considered practically zero. In fact the losses, even of angular grains, are so small that the amount of mechanical rounding in a long river is still negligible. After a succession of ten sedimentary cycles with major stream transport each time, a quartz grain would still remain quite angular, provided no other factor intervened. To reduce a cube of 0.4 mm to a sphere, for instance, would require a river transport of several million kilometers. The much debated question whether there is a lower size limit to mechanical aqueous abrasion, is meaningless. The significant question is whether a distance of transportation can have occurred sufficient to produce mechanically the degree of abrasion shown by a grain of given dimensions. For sand sizes, even the largest, the answer must be in the negative for all but extremely angular grains.

It follows that distinctly rounded sand-size quartz grains have been modelled either by wind, by surf, or by chemical attack. Galloway, following Sorby, suggested that solution is an important factor in the rounding of sand grains. If chemical attack were the main factor one would expect to find roundness inversely proportional to size, and a scarcity of quartz in the silt and clay sizes. Neither of these surmises appears to be true. It is generally accepted that fine sand grains tend to be poorly rounded, in spite of Galloway's contention of the opposite. The hypothesis of solution rounding is therefore not very attractive. But conceivably solvent action occurs while grains stagnate in flood plain deposits. It may well be that alternate chemical attack and small-distance river transport is effective.

Surf action is possibly moderately effective in abrading sand, especially of coarser grades. Twenhofel (1945) concluded from an extensive survey of beach sands that rounding of quartz grains larger than one-half mm is apparently easily done on beaches. However, surf action requires separate experimental

investigation before a conclusion can be ventured. The author intends to undertake such experiments.

The mechanical attack of feldspar sand grains in a river is only about twice as great as that of quartz sand, a value much less than might be expected.

A general conclusion from this investigation is that the presence of feldspar in a sand and angularity of sand grains, even of feldspar, do not provide trustworthy evidence for a short distance of transport.

Experimental investigation of aeolian action has already been carried out and the results will be described in a separate paper.

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DRUMLINS AND RELATED STREAMLINE FEATURES IN THE WARWICK-TOKIO AREA, NORTH DAKOTA*

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ABSTRACT. Northeast-trending drumlins and related streamline features of late Pleistocene age are found in the Warwick-Tokio area of the Devils Lake region of North Dakota. These features range from small drumlins to large ridges or "scorings" in end moraines. Some isolated end moraine patches contain exposures of Pierre shale bedrock of Cretaceous age. These bedrock "highs" seem to have controlled the location of the morainal patches but do not seem significant in the origin of the streamline features. The origin of the streamline features is uncertain but they are probably erosional rather than depositional. Why they are localized in this part of the Devils Lake region and absent elsewhere is not clear. No significant differences of terrain or materials were found among the various parts of the region. Possibly some as yet unknown factor in the now vanished ice is responsible for their formation in this small area.

INTRODUCTION AND PREVIOUS WORK

Drumlins and related large-scale streamline glacial features paralleling

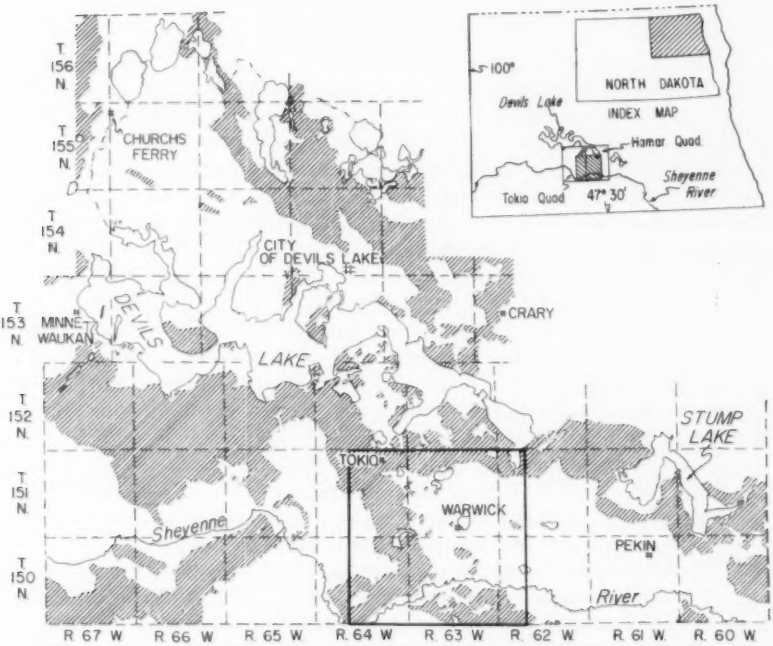

Fig. 1. In upper right, index map of North Dakota showing location of Warwick-Tokio area and the Tokio and Hamar 15-minute quadrangles. Large map shows end moraines in the Devils Lake region. Compiled and edited by Saul Aronow. End moraine areas indicated by diagonal lines. See Aronow (1955) for sources of data. Warwick-Tokio area in heavy outline.

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former ice movement have been only recently noticed in North Dakota (Lemke, 1954 and 1958; Colton and Lemke, 1955; Aronow, 1955). Most of these features are readily apparent only on aerial photographs, which probably accounts for their comparatively late recognition. This paper concerns those in the Devils Lake region of North Dakota near the villages of Tokio and Warwick, mentioned by Colton and Lemke (1955) in their note.

The Devils Lake region in which these drumlins and related features are found was first described and mapped geologically by Upham (1896). His plate XVIII of the Devils Lake region shows moraines only. The Devils Lake region as a whole was later also described by Simpson (1912). The 15-minute Tokio quadrangle in which the western part of the Warwick-Tokio area (see fig. 1) falls was mapped by Easker (1949). Easker's map was later revised and the drumlins added to it by the writer (1955) who also mapped the adjoining 15-minute Hamar quadrangle. Colton and Lemke (1955) noted the occurrence of these features within the area in a general note on their occurrence in North Dakota.

LOCATION AND GENERAL FEATURES

The area, which covers about 144 square miles, is in the western part of Benson County and the northern part of Eddy County, North Dakota. It falls within the Tokio and Hamar 15-minute quadrangles (see fig. 1). The area is in that part of the Central Lowland physiographic province (Fenneman, 1938, p. 559-588) that has been called the Drift Prairie by Simpson (1929, p. 5).

Glacial drift of late Pleistocene age mantles virtually the entire area. Pierre shale of late Cretaceous age everywhere underlies the glacial drift, except where it crops out in a few road cuts and along the trench of the Sheyenne River. The general geology is shown in figure 2; and moraines in the Devils Lake region in figure 1.

Three end moraines cross the area (Easker, 1949; Aronow, 1955). The North Viking moraine, the northernmost, trends eastward and in the northwestern part of the area it merges with the Heimdal moraine. The Heimdal moraine strikes roughly to the southeast and merges with the northeastward trending Hillsdale moraine in the southern part of the area.

Pitted outwash deposits cover considerable portions of the area. The largest of these deposits, located south of the North Viking moraine, covers about one-third of the area. Another, smaller, deposit lies west of the Heimdal moraine. A third deposit can be found south of the Sheyenne River.

The Sheyenne River, in the southern part of the area, flows from west to east. It occupies a trench which, in places, is over one-half a mile wide and over 100 feet in depth. This trench was probably cut during the draining of glacial Lake Souris in the northwestern part of North Dakota (Upham, 1896, p. 267-272). Before the excavation of the trench the glacial Sheyenne River flowed in a series of high-level channels now represented by terraces which flank the trench, and by channels which interlace the moraine south of the trench.

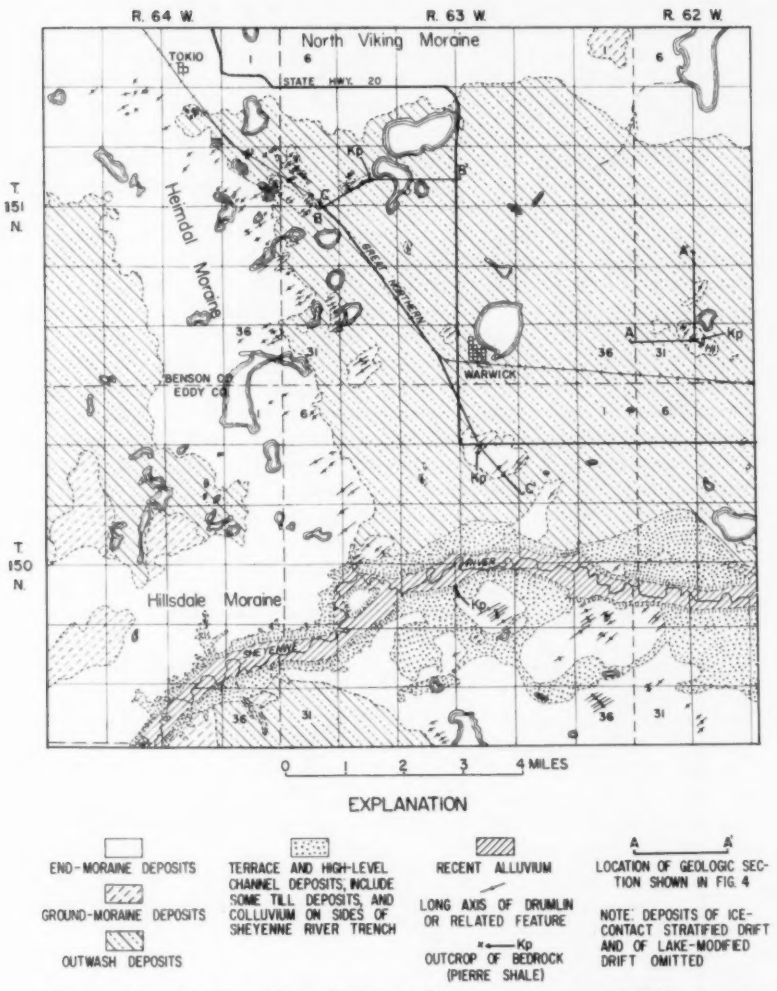

Fig. 2. Map showing geology of Warwick-Tokio area, Benson and Eddy Counties, North Dakota, and location of geologic sections.

DESCRIPTION OF LINEAR FEATURES

The drumlins and related linear features are confined to (a) the Heimdal moraine, (b) its continuation south of the Sheyenne River trench, and (c) isolated end moraine patches, some bedrock cored, completely surrounded by outwash on the proximal side of the Heimdal moraine. In some places in the outwash plain small isolated elongate hills of till rise above the level of the

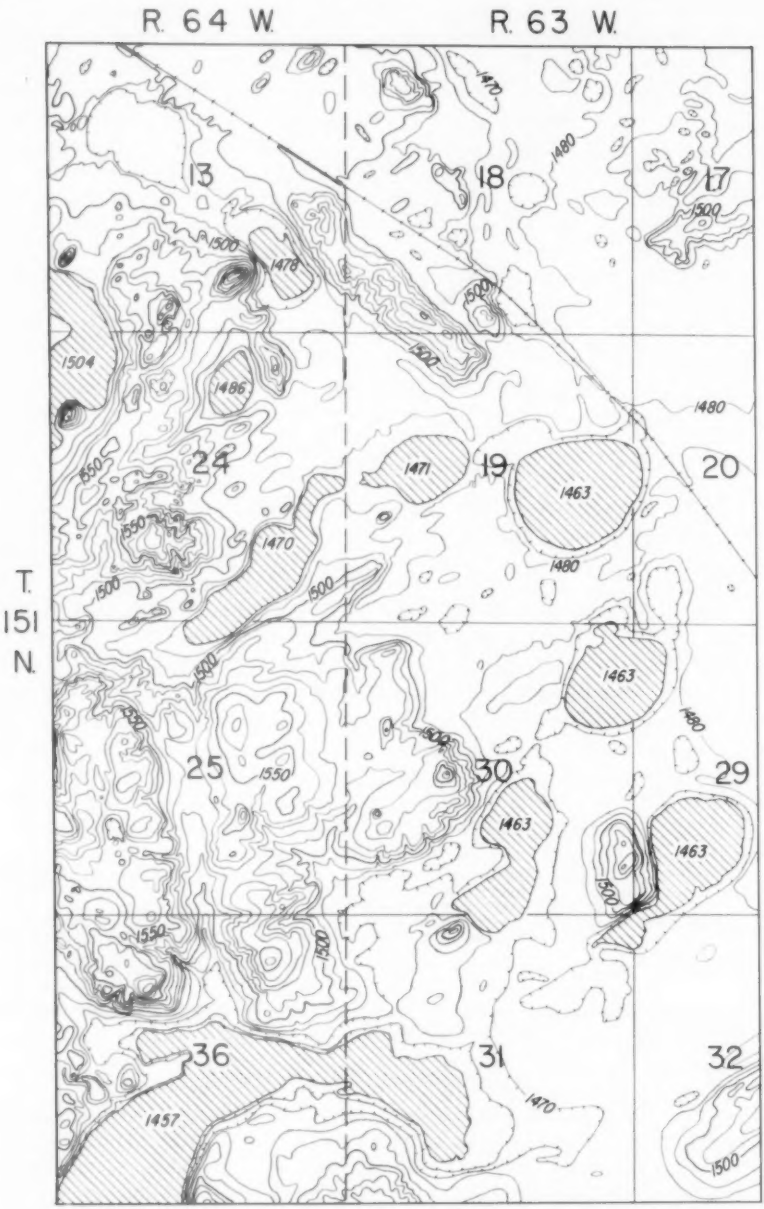

Fig. 3. Topographic map, 10-foot contour interval, of part of Warwick-Tokio area, North Dakota. Traced from the Tokio and Horseshoe Lake 7½-minute quadrangles which cover the eastern half of the 15-minute Tokio quadrangle. Contours simplified in the vicinity of roads; road and swamp symbols omitted.

outwash deposits. These small hills, some of which are drumlin-shaped, were mapped as end moraine because of the occurrence of transitional forms between them and end moraine topography, and because of their till content.

The linear features in the area have a variety of shapes. A small minority have the classic drumlin shape. The bulk of these features, however, fall into a rather nondescript second group which, through transitional forms, make a continuous range of shapes between drumlins and end moraine topography.

Of the approximately 160 shown in figure 2, less than 20 are drmulin-shaped. Most of these are shown in figure 3. They are almost all less than a fifth of a mile long and less than 50 feet in height. Compared with other drumlins, for example, in Wisconsin (cf. Thwaites, 1946, figs. 54 and 55) and New York (cf. Atwood, 1940, figs. 92 and 93) they are rather small. In general, here the smaller the feature the more drumlin-like in form it is.

The individual ridges lacking the drumlin form in end-moraine areas or in isolated hills in the outwash are generally larger than the drumlins. These may be up to about a half a mile in length. Their relief in places may reach 60 feet either in height above the surrounding outwash plain or height above intervening swales. On aerial photographs[1] the ground surface in the places where these are located appears as if it were scored by a gigantic rake which produced elongate ridges and narrow intervening swales. Many of the isolated end moraine patches, when seen in profile, at right angles to the trend of the linear features, have steep stoss slopes and gentle lee slopes although the end moraine mass itself may be elongated parallel to the main trend of the Heimdal moraine. Examples may be found in secs. 31 and 32, T. 151 N., R. 62 W., in SE. ¼ sec. 30 and SW. ¼ sec. 29, T. 151 N., R. 63 W. and in W. ½ sec. 18, T. 151 N., R. 63 W. (see figs. 2 and 3).

Most of the features have strikes that are within the northeast quadrant of the compass. Most strike between N. 40° E. and N. 60° E. Extreme values for strike directions range from N. 14° E. to N. 80° E. Several, however, have strikes that do not fall within the northeast quadrant. These strike to the north and to the northwest and are located in sec. 31, T. 151 N., R. 64 W. and sec. 21, T. 151 N., R. 63 W. (see figs. 2 and 3). Although these few trend more or less parallel to the Heimdal moraine, and perhaps should be considered as just small morainal ridges, they do have the inverted spoon shape. The most puzzling of these is in the SW. ¼ sec. 9, T. 150 N., R. 63 W.; it has the steep slope facing southeast and the gentle slope facing northwest.

The till in this, as in the rest of the Devils Lake region, is a clayey till. Mechanical analyses of till samples collected from other parts of the region, when plotted as cumulative curves on semi-log paper, approximate straight lines. Particle sizes range from clay to boulders. The linear features, except where Pierre shale crops out, are composed of the same type of till.

RELATION OF MORAINAL AREAS WITH LINEAR FEATURES TO BEDROCK

Pierre shale bedrock crops out in road cuts in three of the scored end moraine patches, and in a road cut at the edge of the Sheyenne River trench. The three exposures in end moraine patches are located respectively due west,

[1] An excellent stereopair of part of the area is given in Smith (1943, p. 304). East and West have been reversed on these photographs.

and due south of the village of Warwick, and in sec. 17, T. 151 N., R. 63 W. The exposure at the edge of the trench is on the south side, almost due south of the village of Warwick (see fig. 2).

Several geologic sections (fig. 4) have been prepared using U. S. Geological Survey test hole data, and the outcrops to show the relation of the bedrock to the surface glacial features. Although these sections have considerable vertical exaggeration, they clearly demonstrate the relationship of these particular

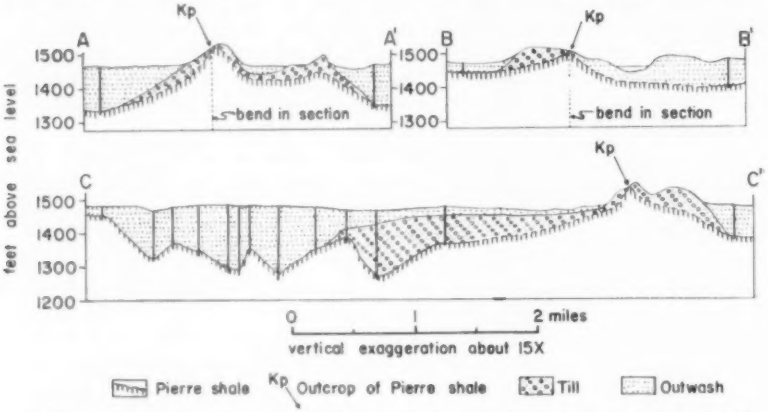

Fig. 4. Geologic sections in the Warwick-Tokio area, North Dakota, based on USGS test hole data. Locations of sections shown in figure 2. Note bends in sections.

end moraine patches to the bedrock. The bedrock, it may be noticed, crops out in at least two of the larger end moraine patches. One is tempted to generalize that most of the other isolated end moraine patches, both north and south of the Sheyenne River are likewise cored with bedrock "highs." This seems to explain the otherwise curious and anomalous patchy and discontinuous distribution of end moraine on the proximal side of the North Viking moraine.[2]

Sections B-B′ and C-C′ have been drawn with the bedrock as a "pinnacle"; the bulk of the morainal patch then consisting largely of drift. The validity of this interpretation is debatable but it seems the safest one. The writer has found that for subsurface data interpretation in the Devils Lake region the best approach is to assume the presence of till unless otherwise indicated.

GLACIAL HISTORY OF THE AREA

The drift in the area is of late Pleistocene age and all the moraines were formed during the retreat of the ice.

The first major halt or readvance of the ice within the area is indicated by the Hillsdale moraine and its modified continuation east of the Sheyenne River. The ice front during this period trended more or less east-west. Probably the stratigraphically lower portion of the outwash in the extreme southern part of the area was laid down at this time.

[2] Upham (1896, plate XVIII) "tied" these isolated end moraine patches together to form a continuous moraine.

The Heimdal moraine marks the next stable location of the ice front, which now trended to the northwest. The gap between the Heimdal and Hillsdale moraines in the western part of the area shows that the ice front must have retreated considerably to the north before pivoting, so to speak, and readvancing from the northeast. Tetrick (1949) and Arorow (1955) suggest that this "pivoting" as well as the merging of the Heimdal and North Viking moraines (see figs. 1 and 2) was caused by the presence of a Pierre shale bedrock "high" in the northwest part of the area which acted as a kind of "bastion" holding up the southward advance of the ice. Farther to the south and east apparently there were no bedrock "highs" of sufficient magnitude to prevent the ice from advancing southward and partly overriding the eastern portion of the Hillsdale moraine. The end moraine patch in secs. 31 and 32, T. 151 N., R. 62 W., with "scorings" more or less perpendicular to the trend of the Heimdal moraine, is almost five miles from the moraine. The ice front must have migrated northward at least to this point before re-advancing to the Heimdal moraine position. The linear features probably were made during this readvance. If not this distant end-moraine patch may have been "scored" in one or more minor readvances during the general retreat from the Heimdal moraine position. The outwash deposits in the western part of the area and the uppermost portion of those in the southern part of the area were laid down during the period when the ice front was at the site of the Heimdal moraine.

The North Viking moraine, in the northern part of the area indicates the last major stand of the ice in the area. The large body of outwash in the central and eastern parts of the area testifies to a lengthy stay of the ice in this position as well as to copious amounts of meltwater. The outwash, in places, is over 200 feet thick. As shown in the geologic sections (fig. 4) some till must have been eroded away by meltwater from the surface now underlying the outwash. Many of the isolated end moraine patches may have been further separated from the main mass of the Heimdal moraine or reduced in size by the activities of these meltwaters. The outwash was then deposited over the partly till-covered, partly bedrock surface, forming a gently southward-sloping plain. Ice blocks, left during the retreat of the ice, were partly or wholly buried by the outwash. They melted, thus pitting the surface of the outwash. The end moraine patches and isolated drumlin-like features were now partly buried, some presumably completely, by this "flood" of outwash.

DISCUSSION

Streamline molded forms, to use Flint's terminology (1957, p. 66), (including, perhaps, small drumlins) are fairly numerous in North Dakota (R. B. Colton, oral communication, 1957). They are generally inconspicuous and difficult to identify from ground view. There are no great drumlin fields in North Dakota comparable say to those of New York or Wisconsin. Charlesworth (1957, p. 391), writing in 1953, says that:

> The conditions necessary for drumlin building were apparently seldom realized: drumlins occupy only a small proportion of the till country. They are rare over vast regions of glaciated Europe, and in North America are infrequent in Pennsylvania and New Jersey and lacking in Ohio, Indiana, Minnesota, the Dakotas and south Michigan.

Whether or not this is true for streamline molded forms in general may be

questionable and awaits the systematic perusal of thousands of the Department of Agriculture's county photo index sheets. Most summary discussions in the literature, with the exception of Flint's (1957, p. 66-72), are concerned with drumlins and tend to ignore the less distinct, less prominent features.

On a local scale, the intriguing problem is why these streamline forms, including drumlins, are present in this particular area, absent from the rest of the Devils Lake region and poorly developed, as drumlins, in the rest of North Dakota. The writer has not come up with any unusual thoughts on the problem but will suggest that revival of the basic idea underlying a generally unacceptable view may be in order. Before delving into the local problem, the writer will review and comment upon some current thoughts on the origin of these features.[3]

On drumlins proper, the traditional diversity of opinion can be placed under two major headings: (a) the depositional, constructional or accretional view, currently accepted by Thwaites (1946), Thornbury (1956) and Charlesworth (1957), among others, and (b) the destructional or erosional view, held at present, in a modified kind of way, by Gravenor (1953) and Flint (1957, p. 66), among others.

The first view is that drumlins were built up under moving ice from drift derived from that ice. Apparently older drift to qualify here must have been reworked to the extent of having its fabric or stratification destroyed. A new form composed of drift with a new fabric was then molded, possibly by the gradual accretion of drift. Thwaites (1946, p. 44-45) has a good point by point discussion and defense of this view.

A variant of this view is a recent suggestion by Hoppe and Schytt (1953) concerning fluted moraine surfaces associated with certain Icelandic and Scandanavian glaciers. The fluting, small ridges, all less than a meter high and less than 200 meters long "may have been formed by the great weight of ice pressing water-soaked moraine . . . up into hollows formed in the lee of boulders." That this process operated on the scale necessary for the formation of large fluted surfaces and drumlins associated with continental glaciers is not known at present. If large scale operation of this process did occur, the form that was molded (or "extruded" like some industrial plastics, as suggested by Flint (1957, p. 71)) may be composed of "new" drift deposited directly from the ice immediately above as well as "old" drift that was reshaped.

The second, the erosional view, holds that drumlins are the carved out or reshaped remnants of drift deposited prior to the advance of the ice. The fabric and stratification in this case would date back to the original deposition of the drift. An analogy to point up the difference between the two views is the difference between the work of a sculptor modeling in clay and one chiseling a form out of rock.

Gravenor (1953) attempts to reconcile the evidence in favor of the depositional view with the erosional view by a "modified erosion theory." His suggestion, in brief, is that the drift, stratified and unstratified, out of which the drumlins were carved was deposited during the advancing and waxing

[3] For a complete and unculled review of the literature on drumlins the reader may consult Charlesworth (1957, p. 389-403).

stage of the ice, largely as "moraines of advance" and associated drift, and later overridden. This ingenious line of argument thus presumably accounts for the diversity of drumlinal material as well as the similarity in age of drumlins and surrounding and underlying drift.[4]

Flint (1957, p. 66), impressed with the varied morphology, size and composition of streamline molded forms ("from 100% bedrock to 100% glacial deposits") says "Obviously those consisting of bedrock are entirely the work of erosion. Those made largely of drift may also be chiefly erosional . . . " He notes the continuum of forms including striations, large groovings, and flutings and drumlins.

What is of most interest here is that Gravenor and Flint point up the fact that hills with the classic drumlin shape are found composed of till, stratified drift, bedrock or combinations of all three. This is significant in relation to the assertion by Thornbury (1956, p. 391) and Thwaites (1946, p. 44) that, among other reasons, drumlins are constructional because they lack the roche moutonnée or stoss-and-lee form characteristic of indisputably eroded bedrock. This difference in form may be a function of the strength of the material or the type of resisitance it offers to erosion: for example, the possibly fine scale removal of massive weak material versus the large scale removal of jointed bedrock by plucking. In a sense, this argument from form is begging the question.

In the late 1930's O. D. von Engeln popularized and extended the views of a German glacial geologist, Flückinger. These views, as expounded by von Engeln (e.g., 1938) are that the attack of glacial ice on bedrock topography is so gross that structural differences in the terrain, as well as the previous topography, exerts virtually no control over the final end product of glacial erosion, namely, the roche moutonnée form. This form, he asserts, is due to something inherent in the motion of the ice: that ice moves in a wave form because of the friction of the moving ice with the underlying bedrock. The powerful undulations of the ice erode the surface into roches moutonnées. The lat Max Demorest (1938), this writer believes, successfully refuted the notions of both the grossness of attack and the wave motion of the ice.

Obviously the shape and lithology of land forms, constructional and destructional, left after the ice disappears from a given region are the result of the interaction of the ice and its load of debris, and the given initial terrain and rocks. Though the cause-and-effect relationships often cannot be clearly differentiated in this interaction we can say that the physical and dynamic condition of the ice is modified by the terrain and rocks, and the terrain and rocks by the ice. For the purpose of discussion an attempt will be made to arrive at a "first approximation" of the factors in the ice that would modify the terrain and rocks, and the converse. Let us consider the following simplified cases: Given two areas identical in topography and geology, each covered by ice advancing from the same direction, any differences in the land forms and materials left by the ice would probably be the result of differences in the glaciers of

[4] About the only one of Thwaites' (1946, p. 44-45) arguments not answered is that of the "reshaped" drumlin.

(1) thickness
(2) velocity
(3) rate of melting
(4) load of debris, sub-, en-, or superglacial.

If the situation were reversed, namely, that two glaciers identical in physical and dynamic condition enter two areas of contrasting topography and materials from the same direction, the ensuing dissimilarity of the areas after the ice left would be due to differences in

(1) topographic "grain" (the orientation of major valleys)
(2) regional slope
(3) texture or roughness of the topography
(4) the resistance of the bedrock or superficial unconsolidated materials to erosion, and the manner in which they can be eroded.

Each of the factors within each group would, to a certain extent, depend on the others. Probably each of the terrain and lithology factors modify each of the glacial factors and vice versa. As far as drumlins and related streamline features are concerned, the physical and dynamic condition of the ice is probably as important as the initial terrain and materials.

Now, with this approach in mind, we will examine the problem of the origin of the drumlins and related features in the Warwick-Tokio area. This area will be compared with other parts of the Devils Lake region lacking in these linear features to find out if anything now seen or inferable about the original topography and materials can be considered significant. Though there is insufficient information available to present a clear-cut and incontrovertible example of the first ideal case (same topography, and materials, different physical and dynamic conditions in the glacier), the writer believes that enough is known to approximate to a surprising degree the conditions necessary for this case. Comparison between the Warwick-Tokio area and other parts of the Devils Lake region will be made under the following heads:

(a) regional slope
(b) topographic grain
(c) character of the drift
(d) configuration of the bedrock
(e) character of the bedrock
(f) topography prior to the last drift.

(a) The bedrock topography on a 250-foot contour-interval map of the central United States by Horberg and Anderson (1956, fig. 1) shows that in a rough sort of way the Devils Lake region lies on the northeast side of a southeast-trending depression. This depression extends below the 1500-foot contour and presumably lies above the 1250-foot depression. Bedrock altitudes, however, less than 1250 feet above sea level were found by test drilling in many places in the Devils Lake region, particularly adjacent to the lakes and in the dry beds of the lakes. This area, under and subjacent to the lakes, may be the lowest place or axis of the depression shown on Horberg and Anderson's map. Thus there may be a reversal of the regional slope within the Devils Lake region which would place the Warwick-Tokio area on the southwestern flank of the depression. Streamline features are absent in other places on this hy-

pothetical flank, which may indicate that the regional slope may not be a critical factor in controlling their formation.

(b) The present surface topographic grain of the Devils Lake region is expressed by the southeast-east orientation of the long axis of the lake complex and the southeast-east to southeast orientation of the moraines that flank the lakes (see fig. 1). Test drilling has shown that in a general way the grain of the bedrock topography more or less parallels that of the surface: the moraines are more-or-less underlain by thin drift or bedrock "highs," and the lowest places in the bedrock flank the lake basins or underlie the dry lake beds. In particular, the southwest-trending moraine north of the city of Devils Lake, with an orientation similar to that of the Heimdal moraine in the Warwick-Tokio area and probably reflecting a similar bedrock topographic grain, has no streamline features associated with it.

(c) The drift in the Warwick-Tokio area, as far as can be seen in numerous road cuts and from numerous drill-hole samples, does not perceptibly differ here from other places in the Devils Lake region which lack streamline molded forms. Factors such as an increased stony or clayey character of the drift, which might cause differences in degree of resistance to erosion, once deposited, or degree of plasticity ("moldability"), thus do not seem significant.

(d) At first glance the configuration of the bedrock in the Warwick-Tokio area seems important. Some of the isolated morainal areas in the outwash are known to be cored with bedrock. Probably most of them are. However, as far as can be determined from road cuts and other exposures in the field, neither the individual flutings nor drumlins seem to have individual cores of bedrock which might have served as starting points for accretion. A gross relationship exists but that is all. The obvious thought here is that the "highs" in the bedrock may have influenced the velocity or local thickness of the ice, possibly critical factors in the origin of these features. But bedrock "highs" are common in other morainal areas in the Devils Lake region as found by test drilling. For example, in a high place in the moraine north of the city of Devils Lake, bedrock was found by test drilling with a cover of drift only about 13 feet thick.

(e) The Pierre shale bedrock, as found in cores and drill cuttings, is fairly uniform from place to place in the Devils Lake region, and like the drift, exhibits no easily discernible differences in the Warwick-Tokio area. Variations in the erodibility of the bedrock are more likely attributable to topographic position rather than changes in the lithology.

(f) The topography just prior to the deposition of the last drift is almost impossible to reconstruct. Ice of several glacial stages prior to the Wisconsin, and several substages of the Wisconsin probably covered the area at different times (see drift border maps in Flint, 1955, fig. 27; 1957, fig. 20-1). Buried weathered zones in the drift, outlining the previous surface, were not found either in surface exposures or in drill hole samples. Presumably any older drift immediately below the latest was at least superficially removed. In the geologic sections (fig. 4) it may be seen that any older drift in many places must have been stripped off down to the bedrock by the erosive action of the ice or flushed out by meltwater. In view of the comparatively small width of

the ridges and drumlins it is unlikely that as yet unobserved centers of accretion of smaller size would have been preserved. An imponderable factor here, though, is the influence of the older topography on the velocity and local thickness of the ice, regardless of the possible preservation of portions of the older drift surface as centers of accretion.

As far as can be determined from the available surface and subsurface information, there seem to be no clearly discernible, critical differences among the glacial and bedrock features in the Devils Lake region that would account for the presence of the drumlins and related streamline features in the Warwick-Tokio area.

The writer would like to suggest that recourse must be had to "something" in the now vanished ice. In working out the origin of drumlins and related streamline features we perhaps should shift the emphasis from the investigation of given rock we can now see to hypothetical conditions in the ice to account for their occurrence. To point up the necessity for reorientation of our thinking, let us consider the fact, discussed previously, that the drumlin *form* seems to some extent to be "available" in a variety of materials, and combinations of materials. Thus molding or extrusion of till may be locally important in their origin. On the other hand, erosion or carving of till, stratified drift, and bedrock may be the dominant processes in some places. Combinations of these processes probably are necessary for drumlins composed of several materials. The suggestion here is that when the conditions within the ice are present for making drumlins and related features they are formed, seemingly, regardless of the materials available. Flint (1957, p. 68-69) says " . . . there is a complete gradation, independent of outward form and within a single field, from rock to drift. This suggests that any one group was molded contemporaneously under a single set of conditions." The continuum of streamline forms would probably indicate variations away from the conditions necessary for the formation of drumlins. Now the writer does not mean to imply that drumlins will be formed regardless of the conditions of the given terrain and rocks, but that when a nice balance between the ice, and the terrain and materials is struck and certain unknown conditions are met, the drumlins will be formed. If the conditions vary other streamline molded forms will be made. The writer would hesitate to extend this idea to the finest members of the continuum, namely striations and small flutings.

Up to now the only hypothesis which has stressed "something" in the ice has been the one of Flückinger's as popularized by von Engeln. This is an unsatisfactory hypothesis. What appears to be needed is a hypothesis of this *type*.

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FACTORS INFLUENCING EROSION OF A COHESIVE RIVER BANK

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ABSTRACT. The sinuous channel of Watts Branch in Montgomery County, Maryland, traverses a grassy meadow nearly devoid of trees. The creek has a drainage area of four square miles and the river bank is composed primarily of cohesive silt. Resurveys of cross sections during the five years 1953-1957 have revealed as much as seven feet of lateral erosion. Over the past two years, additional measurements of the amount of erosion around rows of steel pins driven horizontally into the bank have been made at frequent intervals. These observations indicate several combinations of factors primarily responsible for the progressive recession.

Approximately 85 percent of the observed erosion occurred during the winter months of December, January, February, and March. A thickness of as much as 0.4 feet of sediment was eroded from the bank at specific points in a period of several hours during which a bankfull flow attacked banks which had previously been thoroughly wetted. Erosion was most severe at the water surface. Little or no erosion was observed during the summer despite the occurrence of the highest flood on record in July, 1956.

Second in erosion effectiveness were cold periods during which wet banks, frost action, and low rises in stage combined to produce 0.6 foot of erosion in six weeks during the winter of 1955-56. Significant erosion also resulted from the combination of moist banks and low rises in stage. Lastly, crystallization of ice and subsequent thawing, without benefit of changes in stage, also produced some erosion as did flashy summer floods even on hard, dry banks. Inasmuch as such summer floods constitute the rare and "catastrophic" events on small drainage basins in this region, present observations suggest that the cumulative effect of more moderate climatic conditions on this process of erosion exceeds the effect of rarer events of much greater magnitude.

This preliminary analysis of several factors responsible for erosion of the cohesive river bank indicates that there is perhaps a crude correlation between precipitation and erosion during selected intervals of time. Precipitation exerts an affect both through increasing discharge in the channel and by increasing the moisture in the bank. Frost action acts similarly both to hold moisture in the soil and to comminute surface material, thus preparing it for erosion.

INTRODUCTION AND DESCRIPTION OF THE SITE

The following article is intended to provide a brief description of the method of measurement as well as the results obtained to date in a continuing study of the factors controlling the rate of migration of the channel of Watts Branch near Rockville, Md. These preliminary results and the simplicity of the measurements indicate that additional studies of a similar kind on river banks of varying composition in diverse regions might provide a useful means of studying this erosional process.

Watts Branch has a drainage area of 4 square miles and a width of about 20 feet. In the reach being studied the channel traverses an open pasture largely devoid of trees but covered with grass (fig. 1). Detailed observations of channel erosion are being made at two sections (fig. 3) located on concave banks of the meandering channel. Both sections are downstream from points of maximum curvature of bends.

A resurvey in December 1955 of several cross sections established in 1953 showed rapid erosion. In the 2-year period the banks of the channel in places had receded several feet. Such rapid erosion suggested the possibility of making a detailed study of the primary factors responsible for the erosion. Thus more frequent observations were begun in 1955. In the following analysis data from

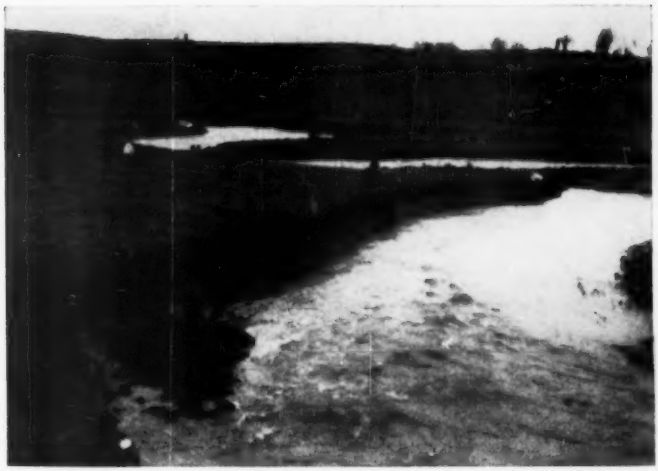

Fig. 1. Reaches measured in bank recession study. Line 1 facing observer in foreground, line 2 background. Flow is from lower right to upper left. Stage is approximately one half bankfull; 3 p.m., January 14, 1958.

these observations are combined with the 5-year record derived from the cross sections used in the long term program.

The bank material is a poorly sorted silt and very fine sand (table 1). The bank exposed during low flow is brown in the upper half and grey in the lower half. Although there is no significant difference in the size distributions of the material at successive levels, several of the physical or mechanical properties show a progressive change from the base of the bank to the surface of the flood plain. Quartz, albite and oligoclase feldspar, muscovite, and kaolinite are the principal mineral constituents. Pertinent descriptive characteristics of the bank material, including moisture content, plasticity index, and unconfined compressive strength, are given in table 1.

METHODS OF MEASUREMENT

The initial study contemplated only resurveys of established cross sections. Measurements of the channel bank confined to a single cross section were considered inadequate, however, for studies of bank recession which occurred during periods much shorter than a year. Therefore, in December 1955 baselines were established on the flood plain approximately parallel to the left bank of the eroding channel at each of 2 measuring reaches (fig. 3). The position of the bank was determined by measuring the perpendicular distance to the baseline at 5-foot intervals. Baseline 1 is 65 feet and baseline 2 is 70 feet long. Measurements were keyed to changes in weather and were made following rain and during cold or dry periods. Experience showed that periodic measurements should also have been made at fixed intervals inasmuch as the determination of the principal cause of the erosion is difficult unless the gaps between times of no erosion and periods of erosion can be properly defined. Measurements from

TABLE 1a

Size Distribution of Bank Material at Watts Branch

Depth below surface of flood plain (ft)	Cumulative percent less than size given (mm)								
	2.0	0.42	0.25	0.074	0.050	0.020	0.005	0.002	0.001
0-1		100	99	83	77	58	29	21	17
1-2		100	99	87	80	57	29	19	16
2-3	100	93	89	79	73	54	30	21	18
3-4 [1]	84	72	66	49	44	31	15	12	10

[1] Core sample included one cobble and several pebbles.

TABLE 1b

Mechanical and Physical Properties of Bank Material at Watts Branch[1]

Depth below surface of flood plain (ft)	Plasticity index	Liquid limit	Shrinkage limit	Shrinkage ratio	Initial density (wet) (lb/cu.ft)	Initial density (dry) (lb/cu.ft)	Strength: Maximum vertical pressure (unconfined) (1000 lb/sq.ft)
0-1	13	44	35	1.50	105	76	0.84
1-2	9	36	31	1.58	.....	.....	.....
2-3	8	31	28	1.66	119	96	2.20
3-4	4	25	24	1.73	123	107	1.83

[1] Analyses generously performed by soils section, Bureau of Public Roads.

TABLE 1c

Moisture Content of Bank Material of Watts Branch

	Depth below surface of flood plain (ft)	Moisture content (percent of dry weight)	Hydrologic conditions before and during time of sampling
Sept. 30, 1957	1	13	3 preceding weeks no precipitation dry at sampling time.
	2	18	
	3	17	
Oct. 6, 1957	1	33	Following 2 days of rain: raining at sampling time.
	2	36	
	3	21	
Dec. 18, 1957	1	38	No precipitation for preceding 7 days: Low temperature.
	2	24	
	3	15	

the baseline contained some error attributable primarily to the difficulty of measuring perpendicular to the baseline. In addition, overhanging turf (fig. 2) made precise location of the position of the bank uncertain.

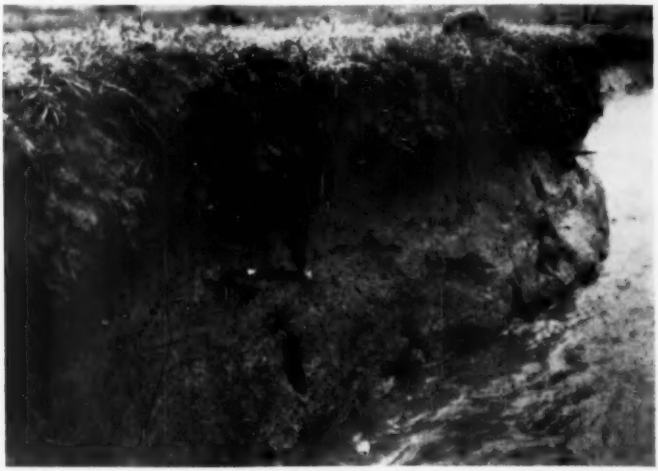

Fig. 2. Close-up of bank of Watts Branch showing sod cover and exposed measuring pin parallel to knife. Erosion of bank by flow of January 14, 1958.

In May 1956, at the suggestion of N. J. King, of the U. S. Geological Survey, the baseline method was replaced by a pin method. Pins 1 foot long and a quarter of an inch in diameter were driven horizontally into the banks approximately 1 foot below the flood plain at the same 5-foot intervals. The painted end of each pin was allowed to protrude 0.05 foot from the bank. Thus *net* erosion is the distance from the head of the pin to the bank minus 0.05 foot. After each measurement the pins were re-driven.

The precipitation and temperature records used are for the United States Weather Bureau gage at Rockville. In the absence of a stream gaging station on Watts Branch, a correlation was made between observed flows of Watts Branch and those at a gaging station 10 miles away on Seneca Creek near Dawsonville. Seneca Creek has a drainage area of 101 square miles at the gaging station. Because of the difference in size of drainage basin the correlation is only fair, but the flow record has proved adequate in relating the observed erosion at Watts Branch to its regimen of flow.

Believing that the level of ground water in the flood plain adjacent to the eroding bank might affect the amount of erosion, three wells, each approximately 3.5 feet deep, were installed at 7-foot intervals on a line perpendicular to the eroding bank at base line 1 (fig. 3). Intermittent measurements of stage in the wells during both dry and wet periods have shown that at all stages the gradient of the water table is toward the stream, the gradient being less at high stages than at low. No reversals have been observed. The data are too few to permit further analyses and are not included in this discussion.

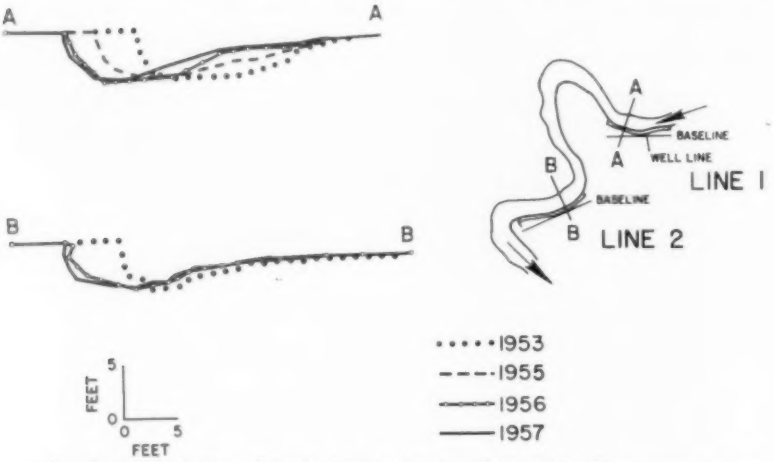

Fig. 3. Map of Watts Branch showing location of measuring lines, cross sections, and well line, and successive amounts of erosion in cross sections.

OBSERVATIONS AND POSSIBLE EXPLANATIONS OF DIFFERENCES IN ANNUAL EROSION

Figure 3 shows the results of resurveys of cross sections A and B over a period of 4 years. In both sections 6 feet of material has been removed from the concave bank. Due to deposition on the opposite bank the width of the low water channel has remained constant. Cross section A also shows that the amount of erosion between 1953 and 1955 far exceeds the amount since 1955.

The actual periods of erosion and non-erosion along baselines 1 and 2 are more strikingly illustrated by the graph in figure 4 showing the cumulative amount of erosion with time for the first 2 years of detailed measurements. Despite variation in the amount of erosion around individual pins, the amount of erosion at each pin between successive measurements on each line and the rates and times of erosion on the two lines are in general agreement. The variation observed between individual pins is not sufficient to destroy the obvious relation between lack of erosion in summer and marked erosion in winter. It is clear from figure 4 that during the two years of record most of the erosion occurs during the months of December, January, February, and March. This has proved to be true also during the winter of 1957-58. During the summers of 1956 and 1957 little or no erosion was recorded.

The measurement in July 1956 on line 1 is of particular interest. The highest flood on record in this area occurred on July 20. At Watts Branch the stage was approximately 2 feet above bankfull. Despite the volume of flow and its stage, erosion around the pins was negligible compared to the erosion regularly observed during the preceding and following winters.

The graphs (fig. 4) also show that the winter of 1955-56, including the months of December, January, February and March, produced more erosion

than the same period in the winter of 1956-57. Mean cumulative erosion at all pins on line 1 is 1.7 feet from December 5, 1955 to June 1957, whereas the mean cumulative erosion in line 2 is 1.2 feet. Subsequent erosion in December 1957, and January 1958, has increased these figures to 2.3 feet and 1.5 feet on lines 1 and 2 respectively. A comparison of the progressive erosion at the two lines indicates that save for the periods December 12, 1954, to January 15, 1955, and December 20, 1957, to January 20, 1958, the periods and amounts of erosion in the two have been parallel. No explanation has been found for the differential erosion observed during these periods although recent observations (see below) suggest that it may be related to the angle of attack of the flow.

The data (fig. 4) show that the gross annual differences in amount of erosion seen in the cross sections (fig. 3) must have been the result of winter climatic and flow conditions. In an attempt to explain these differences, accumulated precipitation and accumulated fluctuations of temperature about the freezing point (using daily maximum and minimum temperatures) were studied for the four winters from 1953 through March 1957. Each winter period included the months December through March. Although the differences in total precipitation and in the total number of fluctuations about the freezing point between successive winters are small, a comparison of December and January for the two winters 1953-54 and 1954-55 with these same months in 1955-56 indicates that a higher precipitation might have been responsible for the higher rate of erosion during these first 2 years. That precipitation alone is responsible is suggested by the fact that the fluctuations about the freezing point were actually more numerous during 1955-56, the year of least erosion. The significance of precipitation alone, however, is not borne out in the comparison of the winter of 1955-56 with 1956-57. Precipitation was considerably greater in December, January, and February 1955-56, yet the annual erosion (fig. 3) was less than in the following year. Consideration of these two important factors alone is thus inadequate to explain the gross annual differences observed in the successive cross sections.

Assuming that cumulative temperature deficiencies in degree days rather than fluctuation around the freezing point might better characterize the severity of frost conditions during a given period of time, deficiencies were computed for the winters 1953-54 through 1956-57 by cumulating the differences between the mean temperature and 32°F for each day that the mean was lower than 32°F. Although some relation between temperature deficiencies, precipitation, and erosion was apparent for the three winters, annual periods proved to be too long for detailed analysis.

OBSERVATIONS AND POSSIBLE EXPLANATIONS OF DIFFERENCES IN EROSION IN SHORT INTERVALS OF TIME

The variety of combinations of factors producing erosion of the river bank can be seen better by examining concurrent records of erosion and climate for several winters. Figures 5 and 6 show precipitation, discharge, daily mean temperature, and mean erosion at lines 1 and 2 for the winters 1955-56 and 1956-57. On the erosion scale the vertical lines represent the

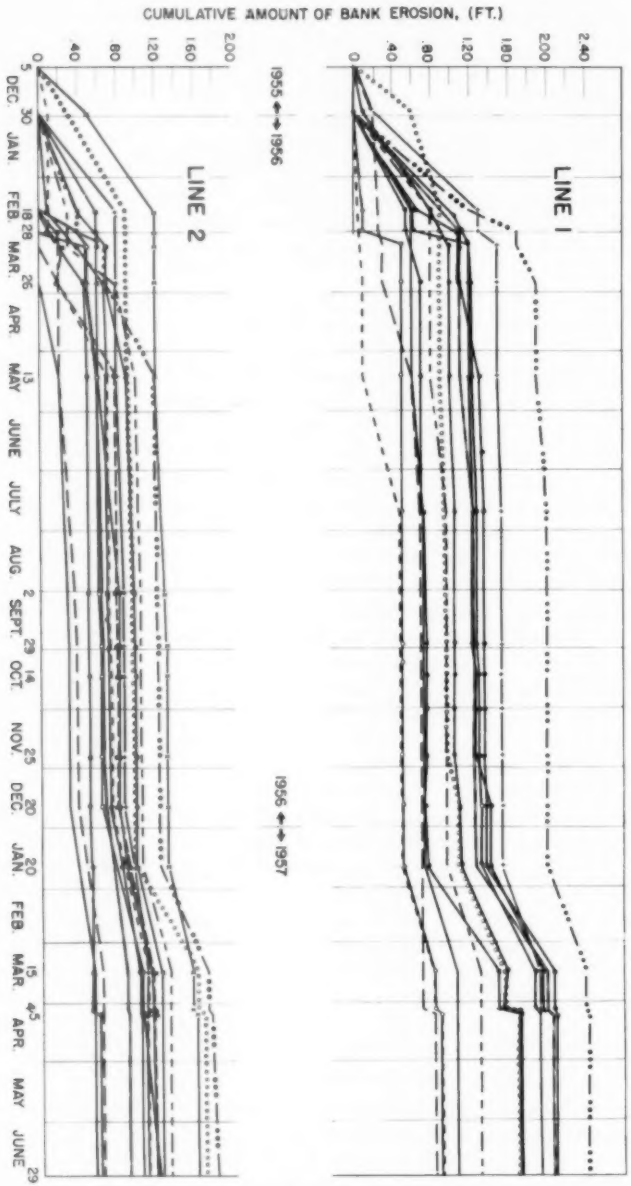

Fig. 4. Cumulative bank erosion on lines 1 and 2 from December 1955, through June 1957.

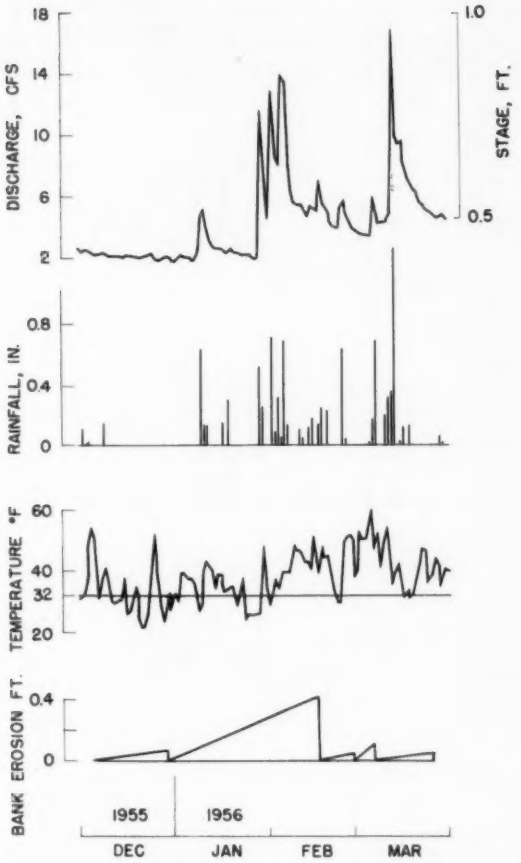

Fig. 5. Concurrent records of discharge, precipitation, mean daily temperature, and bank erosion for the winter 1955-56.

mean amount of erosion observed at the time of measurement. The diagonal lines drawn to the peak of the individual measurements indicate the period of time over which the erosion took place. They do not indicate that erosion was uniformly distributed throughout the intervals. For ease of later references the record is summarized chronologically in table 2 and particular sets of conditions are numbered successively throughout the 2-year period.

By sorting out the combinations of conditions shown chronologically in figures 5 and 6 and summarized in table 2 it is possible to give some indication of the relative importance of several of the factors studied and perhaps some qualitative explanations of their rank.

It is clear that maximum erosion results when high flows attack banks

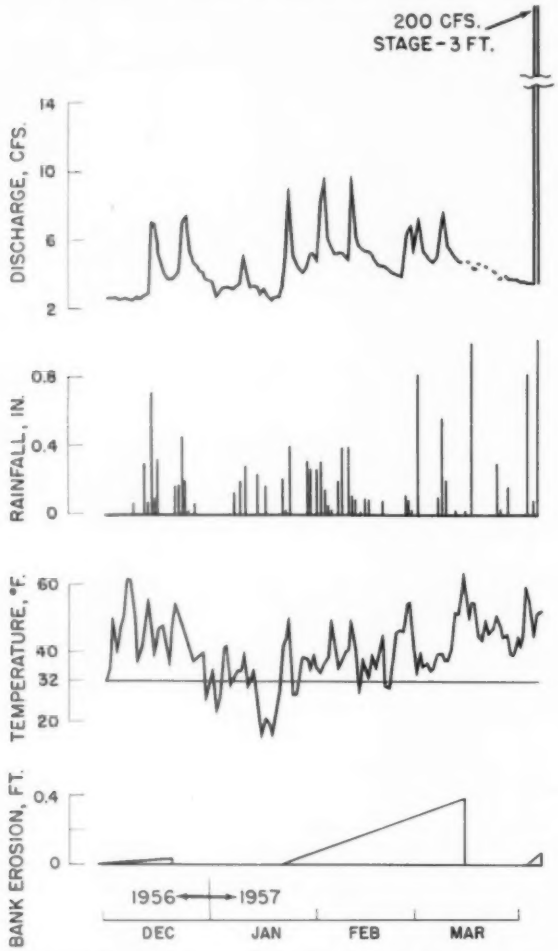

Fig. 6. Concurrent records of discharge, precipitation, mean daily temperature, and bank erosion for the winter 1956-57.

already thoroughly wetted (conditions 2 and 7, table 2). The inclusion of the word "thoroughly" is apparently required by the fact that rapid rises in stage which occur during the summer are not sufficient to "thoroughly wet" the banks in the manner or degree to which they are wetted during the winter. The flow of April 5, 1957 (condition 8) illustrates this. Erosion during this flow considerably exceeded that produced by the much larger record flood of July 20, 1956, and must be attributed to the wet condition of the banks in the spring in contrast to their dry hard state in summer. (Some differences in moisture

TABLE 2

Combinations of Climatic Factors Associated with Erosion of Streambank at Watts Branch During the Winters 1955-56 and 1956-57

Condition	Winter	Measurement Interval	Precipitation	Discharge and Stage	Temperature	Mean amount of bank erosion (ft)	Remarks
1	1955-56	December 1955	low	no rise in stage	daily mean below freezing ½ of month	0.07	Minimum winter erosion produced by frost without increases in stage
2		January 1 to February 16, 1956	moderate greater than above	several low rises (1 ft)	several days of freezing	.41	Maximum cumulative erosion
3		March 1 to March 9, 1956	one rain	one 1 ft rise	no frost	.12	contrast with condition 1, here no frost, moderate rise, erosion 2.
4		March 9 to March 26, 1956	considerable	moderate stage	few days of frost	.05	
5	1956-57	December 1 to 20, 1956	considerable	1 rise in stage	well above freezing	negligible	
6		December 20 1956 to January 19, 1957	low	few rises	low temperature	negligible	
7		January 20 to March 16, 1957	high	several low rises (1 ft)	occasional day below freezing	.38	Maximum erosion similar to condition 2.
8		April 5, 1957	heavy and intense	3 foot stage	high	.07	erosion at 4 pins greater than 0.20 foot.

content are shown in table 1). Erosion in the April flow occurred in the absence of frost in the ground. Because of irregularities along the banks and resulting irregularities in the water surface during the April flow some of the pins were equal to, slightly below, or a few inches above the maximum elevation of the water surface. Streaks and occasional cup-size potholes in the bank show that the material was sheared off by the flow and did not simply fail or collapse. No sediment was removed from around the pins above the water surface. From previous measurements at this stage, point velocities in a horizontal plane several feet above the bed are known to vary approximately logarithmically from 1.5 fps at a distance of 0.4 feet to 2.5 fps at a distance of 1.3 feet from the bank.

Several recently observed flows during the winter of 1957-58 also provide good illustrations of the effectiveness of high flows in eroding wet banks. During each of these flows the stage rose to within 0.5 foot of the top of the bank. The amount of erosion was measured after two high flows in late December and again following a rise on January 14. As table 3 shows, erosion on line 1 exceeded that on line 2 in both cases. During the highwater of December 20 the flow at line 1 appeared to the author to be more turbulent and to impinge more directly against the bank than it did at line 2. These factors may be responsible for the differential erosion on the two lines. In both reaches, however, several point velocities measured 0.5 foot below the water surface and 0.5 from the bank exceeded 3 feet per scond. During the same flows point velocities near the bank in straight reaches measured 1 foot per second or less.

In contrast to April 1957, the temperature was low during the period in which these flows occurred and it appears that the increased erosion may be attributable in part to frost action. It is also clear, however, from the association of erosion with the flow distribution at several points that the principal agent producing the erosion occurred at locations where the flow was concentrated as it moved around protrusions in the bank. Similarly, as the flow expanded downstream from these protrusions, erosion was reduced. Had frost action dominated the erosion process, more uniform erosion at each pin might have been expected.

Next in erosion effectiveness to intermittent high flows on wet banks are periods in which freezing and below freezing temperatures are followed or accompanied by moderate rises in stage (conditions 2 and 7). During such rises the flow readily removes from the base of the bank granules loosened by frost action and the loose, unsupported sediment from above falls of its own weight. Because the formation and growth of the frost crystals is enhanced by the presence of added moisture available in the soil, freezing and thawing are perhaps very effective in removing sediment during these cold, wet periods. The effect, however, is not separable in this study from the concurrent effect of the moderate rises in stage. The accumulated erosion produced under the above winter conditions has actually accounted for the largest part of the total erosion because of the comparative infrequency of the higher or bankfull stages.

It is interesting to note that an analysis of the annual distribution of the total suspended load transported in three rivers, two in the Piedmont region of eastern Pennsylvania and one in North Carolina, showed that approximately 65 percent of the sediment was transported during the months of November, December, January, February, and March. This period coincided in general with the period during which the largest percentage of the total volume of flow occurred. In these rivers much of the measured sediment is probably derived from the upland suggesting that the same factors which contribute to erosion of the river bank also promote erosion on the upland.

The moderate rises in stage of March 14-15, 1956 (condition 4), indicate that without benefit of preparatory frost action the effectiveness of individual rises is reduced. The combination of moderate stages and wet banks in the absence of frost action then provides a third roughly defined condition of erosion effectiveness.

TABLE 3

Bank Erosion at Lines 1 and 2 at Watts Branch Following High Flows of December 21 & 26, 1957, and January 14, 1958

Station	December 26, 1957		January 19, 1958	
	Line 1 feet	Line 2 feet	Line 1 feet	Line 2 feet
0	0.20	0.00	0.48	0.03
5	.23	.00	.36	[2] .00
10	.06	.23	.25	[2] .00
15	.02	.13	.43	.13
20	.28	.07	.10	.23
25	.38	.08	.17	.26
30	.40	.20	.27	[2] .00
35	.28	.03	.70	.37
40	.30	.11	.62	.23
45	.23	.25	[1] 1.00	.23
50	.12	.10	.58	.15
55	.09	.23	[1] 1.00	.43
60	.28	.27	.77	.17
65	.40	.18	[1] 1.00	.30
70		.12		[3]

[1] Pin missing, possible erosion 1.0 foot, not included in computation of mean.
[2] Covered with sediment.
[3] Covered or missing.

The month of December 1955 (condition 1), illustrates a fourth category in which some material is removed from the banks by frost action alone. Particles are heaved out from the bank by ice crystals and upon melting of the crystals the sediment drops into the stream. Sediment particles produced in this way have been observed on ice which occasionally rimmed the low water channel during the winter.

When winter observations were first begun, the striking growth of ice crystals on the bank led the author to suppose that frost action was a predominant factor in producing bank erosion. During intensely cold periods slabs of sediment perhaps one foot square containing thin ice lenses have been observed. The action of frost appears to be one of preparation of a veneer of sediment for erosion as well as increased retention of moisture in the soil. Because of the complex interaction of the many factors involved, it has not yet been possible to make an adequate correlation illustrating the relative significance of the many factos contributing to erosion. In figure 7, however, an attempt was made to correlate precipitation and temperature with erosion. The position of each point in the figure is defined by the average bank erosion in the two reaches during an interval between successive measurements and by the total precipitation during the same period. The numbers beside the points show the percent of days during the interval in which the daily mean temperature was below freezing. Although in general erosion appears to have some

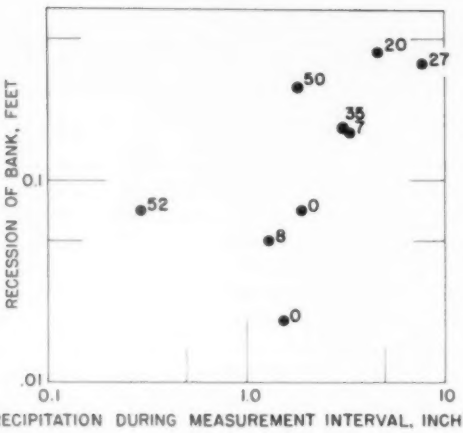

Fig. 7. Relation of erosion to precipitation and frost. Numbers refer to percent of days in interval mean daily temperature was below freezing.

relation to precipitation, the data in the figure suggest that considerable erosion in some periods may be attributable to freezing temperatures. The relation in figure 7, however, as well as the discussion of differential erosion during the flows of December 1957, suggest that precipitation through its effect on both soil wetting and stage is the most significant factor in promoting erosion of the stream bank.

The evidence gathered thus far indicates that lateral migration of Watts Branch by erosion of the banks takes place primarily during the winter. Inasmuch as the maximum floods on record on small drainage areas in this region are the result of summer and fall thunderstorms, it appears that this particular erosion process is associated with what might be termed "moderate" climatic events of frequent occurrence rather than with "extreme" and infrequent events. To the author, at least, the observed rates of erosion appear to be unexpectedly high. The banks being studied are in an unusually sinuous reach (ration of channel distance to valley distance is 1.9) without trees, and the question arises as to the extent to which the presence of trees would inhibit the formation of meanders and the rate of lateral migration. It is certain that if the observed rate of erosion of 1.5 to 2.0 feet per year were the rule in this region, numerous bridge abutments and gaging stations would long since have fallen prey to the rivers on which they are built.

ACKNOWLEDGMENTS

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THE SOLUBILITY OF CARBON DIOXIDE IN WATER AT HIGH TEMPERATURES

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ABSTRACT. There are few results available in the literature for the solubilities of gases in water over 100°C, and for the geologically important gas carbon dioxide there is no information. In this paper the presentation and interpretation of high temperature gas solubilities is discussed, and values are reported for the solubility of carbon dioxide in water up to 350°C. The anomalous behavior of water compared with other liquids as a solvent for gases is reviewed briefly.

Extrapolation of solubility data from low temperatures can be completely misleading unless it is realized that gas solubility coefficients pass through minimum values, usually in the temperature range 70° to 200°C.

INTRODUCTION

In the investigation of many natural hydrothermal processes, a knowledge is required of the solubility of carbon dioxide in water above 100°C. The pH of many hydrothermal solutions is controlled by the buffer system bicarbonate-carbon dioxide, and the conditions for the deposition of many minerals, especially carbonates and sulphides, are defined in turn by the pH of the solutions.

Detailed information on the system $CaCO_3$—CO_2—H_2O was given by Miller (1952), but his experiments were terminated at 100° because information was not available on the system CO_2—H_2O at higher temperatures. Results are given below for the solubility of carbon dioxide in water up to 350°C. In two further papers, the equilibrium condition in the system Na_2CO_3—$NaHCO_3$—CO_2—H_2O up to 220°, and the solubility of calcite in carbon dioxide solutions up to 300° will be reported.

RESULTS REPORTED FOR OTHER GASES

There has been little work on the solubilities of gases in water over 100°C. Before 1952, results available were for ammonia up to 150° at partial pressures of gas from 0.01 to 10 atmospheres (Clifford and Hunter, 1933), for nitrogen up to 240°C at pressures of 100, 200 and 300 atmospheres (Saddington and Krase, 1934), and for hydrogen up to 220° at 31 to 116 atmospheres (Ipatieff and Teodorovich, 1934).

Pray, Schweickert and Minnich (1952) reported the solubilities of O_2, H_2, N_2, He and A up to about 340° with partial pressures of gas approximately equal to that of water vapor. Henry's Law was obeyed within the accuracy of their experiments (about ±5%) to at least 35 atmospheres for the gases examined.

The Henry's Law coefficient does not remain constant at high gas pressures of the order of hundreds of atmospheres, but an improvement is noticed at higher temperatures (Saddington and Krase, 1934). These workers found an almost linear relationship between the partial pressure of nitrogen, p_{N_2}, and its mole fraction in solution, x_{N_2}, up to 300 atmospheres at 240°.

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METHODS OF EXPRESSING GAS SOLUBILITY

The results from gas solubility or distribution measurements at constant temperature are usually expressed by means of one of the following coefficients. β (mean Bunsen absorption coefficient) is the volume of gas (measured at N.T.P.) dissolved in one volume of solvent, when free of gas, divided by the partial pressure of the gas in atmospheres.

λ (Ostwald coefficient) is the fraction

$$\frac{\text{grams gas/cc. liquid phase}}{\text{grams gas/cc. vapor phase}}$$ (as defined by Saddington and Krase).

$K = p_g/x$ (Henry's Law coefficient). p_g is the partial pressure of the gas, and x is the ratio of the moles of gas to the sum of moles of gas and water in solution.

The coefficient β was designed originally for interpreting solubilities at room temperatures where the concentration of water in the gas phase is small. In the presence of a steam phase of moderate density it is often convenient to use distribution coefficients of the Ostwald type. In the present work two other distribution coefficients are used. These are defined below.

(1) $A = \dfrac{n^l_a/n^l_{H_2O}}{n^v_a/n^v_{H_2O}}$, where n_a is the number of moles of gas (a), and n_{H_2O} the number of moles of water in the liquid (l) and vapor (v) phases.

(2) $D = x^l_a/x^v_a$, where $x_a = n_a/(n_a + n_{H_2O})$ in the liquid and vapor phases.

(3) It can be shown that $D = A\,[1 + (n^v_a/n^v_{H_2O})(1 - D)]$ where the value of $(1 - D)$ is close to unity, except at temperatures approaching the critical point. When p_a is very much less than p_{H_2O}, D is approximately equal to A.

β and K relate the *amount* of gas dissolved in the liquid to the partial pressure (or better, the fugacity) of the gas in the vapor phase, while λ, A, and D express the *distribution* of the gas between two phases.

The Henry's Law coefficient is equivalent to $K = p_a/x_a = P/D$, where P is the total pressure of the system, water + gas. The partial pressure of a gas is defined by the equation $p_a = P.x_a$. This will not be the actual pressure exerted by molecular species (a) unless the gas mixture is ideal. To obtain the chemical potential μ of (a) from the equation

$$\mu_a = \mu_a^{\circ}(T) + RT \ln p_a\alpha_a$$

the fugacity coefficient α_a must be evaluated. α_a incorporates all the deviations from ideal behavior caused by gas imperfections and interactions.

The coefficients A and D are useful for showing the distribution of small amounts of gas between water and steam phases. This situation is often met with in geological systems. Along with the Ostwald coefficient they have the advantage of becoming equal to unity at the critical temperature of the mixture, but they become insensitive as an indication of gas distribution at high gas pressures.

$$D = \frac{P}{K} = \frac{p_{H_2O} + p_a}{K}$$

If K is assumed to remain constant with variations in pressure, when p_a is very much greater than p_{H_2O}, D becomes approximately proportional to the pressure of the gas and therefore of little value.

The relationship of A to β is given by the equation

$$A = \frac{\beta . M_{H_2O} . p_{H_2O} . \rho^{o}_{a}}{M_a . f_{H_2O} . \rho^{1}}$$

M_a and M_{H_2O} are the molecular weights of (a) and water, ρ^1 the density of the liquid phase, ρ^{o}_{a} the density of the gas (a) at 0°C and 1 atmosphere, and f_{H_2O} the weight fraction of water in the liquid solution.

The coefficients β and λ show minima for many gases at temperatures in the vicinity of 100°. An example is the solubility of nitrogen at 100 atmospheres pressure (Saddington and Krase, 1934). The actual temperature of maximum solubility depends on the solubility coefficient used.

TABLE 1

T°C	50	65	80	125	180
100β	1.10	0.96	0.95	1.13	1.45

The Henry's Law coefficient K for each gas shows a maximum with increasing temperature. At the critical temperature of the mixture, K = P (total pressure).

Weight distribution coefficients such as A or D do not show minimum values with increasing temperature, but increase continuously up to the critical point distribution of unity. The distribution of gas between liquid and vapor changes rapidly just below the critical region due to rapid changes in the structure of water.

If the values of the solubility or distribution coefficients are extrapolated to zero gas pressure, constants (e.g. K^o, A^o, or D^o) are obtained for a gas at each temperature. It is considered that the constants at zero gas pressure provide the best measure of the solubility of a gas in a liquid, or its distribution between two phases. Values at high gas pressures emphasize factors arising from imperfect gas behavior. At zero gas pressure the coefficients A and D become equivalent.

In figure 1 (from Ellis and Fyfe, 1957) a plot of log D^o versus log (ρ^v / ρ^l) is given for various gases for which experimental data are at present available. Lines of slight curvature from room temperatures up to the critical temperature are obtained. The density of a phase seems to be the factor controlling most vapor-liquid distributions. Styrikovich, Khaibullin, and Tshvirashvili (1955) found that the coefficient, A, for the distribtuion of SiO_2 NaCl, $CaCl_2$, and Na_2SO_4 between vapor and liquid water phases was related to the density, ρ, by the following relationship

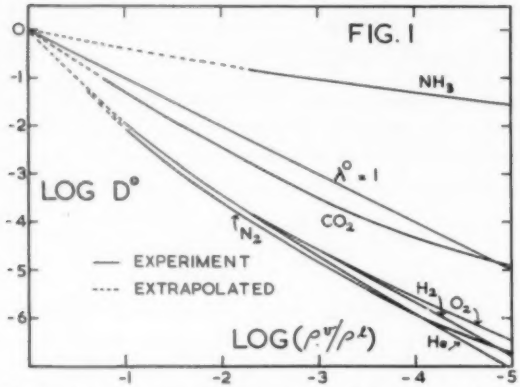

Fig. 1. Distribution of various gases between liquid and vapor phases of water up to the critical point.

$$A = \left(\frac{\rho^v}{\rho^l} \right)^m$$, where m is a constant for each substance.

From this type of graph it is possible to predict the approximate high temperature solubilities of gases from values below 100°C. In figure 1, $\lambda^o = 1$ is given as a line of reference. Along this line the mass of gas is the same in unit volumes of both liquid and vapor.

CO_2 SOLUBILITY AT LOWER TEMPERATURES

The two most important sets of results are those of Zel'venskii (1937) and Wiebe and Gaddy (1939, 1940). These workers reported values for carbon dioxide solubilities up to 100° at gas pressures ranging from 25 to 700 atmospheres. In table 2 the values reported have been extrapolated to zero gas pressures and values of K^o, and A^o or D^o obtained. The agreement between

TABLE 2

T°C	Source*	K^o (at.) (Henry's Law)	D^o or A^o $\times 10^6$	$P = p_{H_2O}$ (at.)
0	Z	680	8.9	0.00603
18	W	1450	14.0	0.0203
25	Z	1640	19.0	0.0312
31	W	2000	22	0.0442
50	Z	2870	42	0.121
50	W	2980	41	0.121
75	Z	3900	98	0.380
75	W	4230	90	0.380
100	W	5270	190	1
100	Z	5150	195	1

* Z = Zel'venskii, W = Wiebe and Gaddy.

the solubility values reported by the two workers is usually better than ± 5 percent. Wiebe and Gaddy's results were obtained by a rather more satisfactory technique.

An abstract of Zel'venskii's paper stated that a "corrected thermodynamic form of Henry's Law" was obeyed to 30 atmospheres at 25°, 55 atmospheres at 50°, and 95 atmospheres at 100°C. The original was not available but this presumably refers to Henry's Law applied to the un-ionized fraction of carbon dioxide in solution.

APPARATUS AND PROCEDURE

Saddington and Krase (1934) analyzed both the liquid and vapor phases in equilibrium with a continuous stream of high pressure gas. Wiebe and Gaddy (1939), and also Pray, Schweickert and Minnich (1952) analyzed the liquid phase only and recorded the total pressure of gas + water vapor. This is satisfactory only at high gas pressures. Wiebe and Gaddy (1941) later determined the solubility relationships in the vapor phase of the system CO_2—H_2O.

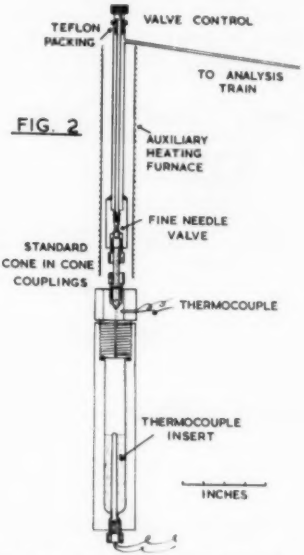

Fig. 2. Bomb with sampling valve.

In the present investigation the apparatus shown in figure 2 was used. A system of known composition was contained in a stainless steel bomb of approximately 100 cc capacity. The liquid volume was approximately half to two-thirds of the total bomb volume at the temperature of the experiment. The whole assembly up to the lead-off tube to the analysis train was heated in a 3″ diameter electric tube furnace. The temperature gradient between the thermocouple inserted in the liquid and the one in the bomb head was usually about

2-3°, the top being hotter. Stainless steel was used for all parts except the lead-off tube which was silver.

The vapor phase was sampled through a needle valve capable of fine control. It was necessary to maintain the sampling valve assembly at a higher temperature than the bomb (about 10-20°) by means of an auxiliary furnace to prevent condensation of the steam sample. The valve chamber was sealed and vacuum tight.

A known mixture of carbon dioxide and water was generated in the bomb by the reaction of sodium bicarbonate with hydrochloric acid. Known amounts of water and bicarbonate were placed in the bomb, and standard hydrochloric acid placed in a thin-walled 7 cc stainless steel tube which was too wide to fall below the top of the thermocouple insert. The bomb-head and valve were connected, the bomb quickly evacuated, and the assembly was then inverted and agitated to ensure complete mixing of the acid and bicarbonate solutions.

Preliminary experiments showed that if the apparatus was maintained at a temperature overnight this was sufficient time for equilibrium to be established between the liquid and gas phases.

A fraction of the vapor phase (about 10 percent of the phase) was then sampled. The sampling train is shown in figure 3. With valve 2 closed and the remaining valves open, the sampling train and the valve chamber were evacu-

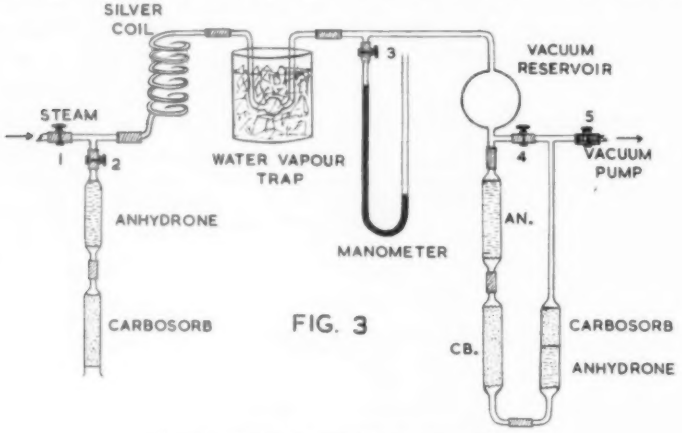

Fig. 3. Train for analysis of steam phase.

ated. Valves 3, 4 and 5 were then closed, and a sample of steam allowed to escape from the bomb in a single burst lasting only about a second. The water-vapor trap in an ice-salt mixture, and the silver coil which was also cooled, collected almost all the condensed steam. Condensation did not occur until the steam reached the silver coil as the lead-off tube was short and was kept at about 100° until after valve 1. Valve 5 was opened and the system again evacuated, thus pulling most of the carbon dioxide through the Carbosorb tube (CB). Valves 1 and 5 were then closed and valve 2 opened slowly. With valve 5 opened slightly, air purified from water and carbon dioxide was pulled

through the apparatus through valve 2 for about 30 minutes to ensure that all the carbon dioxide from the sample was collected in the Carbosorb. The water in the traps and Anhydrone tube (AN), and the carbon dioxide in the tube (CB) were then weighed. In this way the weight ratio of carbon dioxide to water in the steam phase was obtained.

Sufficient acid was added to react with rather less than half the bicarbonate present. It was found that a solution of carbon dioxide and sodium chloride caused appreciable corrosion in the bomb, whereas with an approximately equimolar mixture of bicarbonate and carbon dioxide corrosion was negligible. A small correction was necessary for the dissociation of the bicarbonate remaining in solution by the reaction

$$2HCO'_3 \rightarrow CO_3'' + H_2O + CO_2$$

Information on this reaction is reported in the second paper of this series.

Allowance was made for the increase in volume of the bomb due to thermal expansion. The bomb volume was 97.3 cc, measured at 20°C with the tube for HCl in place. The volume was estimated for other temperatures by taking the coefficient of linear thermal expansion of stainless steel as equal to 1.0×10^{-5} deg. $^{-1}$.

The volume of the solution at a temperature was obtained from its volume at 20° by multiplying by the density (ρ) ratio for liquid water $\rho^{20}{}_{H_2O} / \rho^{T}{}_{H_2O}$ obtained from the steam tables of Keenan and Keyes (1936).

A typical experiment is worked through in detail below.

T = 257°C	$NaHCO_3$ added	= 1.680 g
	(purity 99.7% remainder assumed Na_2CO_3)	= 0.0200 moles
	HCl added	= 0.00797 moles
Volume solution 20°		= 52.75 cc
Volume solution 20° corrected for H_2O in steam		= 52.04 cc
Volume solution 257°		= 65.9 cc
Volume bomb 257°		= 98.0 cc
Volume steam phase		= 32.1 cc
Wt. water in steam sample		= 0.0629 g
Wt. CO_2 in steam sample		= 0.0174 g
Ratio $n^{v}{}_{CO_2} / n^{v}{}_{H_2O}$		= 0.1131
Density of pure sat. steam, 257°		= 0.0225 g/cc
Density of sat. steam over solution (lowering of vapor pressure by ions)		= 0.0222 g/cc
Wt. water in vapor phase		= 0.713 g
Moles water in vapor phase		= 0.0396
Moles CO_2 in vapor phase		= 0.00448
Moles CO_2 due to acid		= 0.00797
Total CO_2 corrected for HCO'_3 decomposition		= 0.00805
Moles CO_2 in liquid		= 0.00357
Moles water in liquid phase		= 2.850
$n^{l}{}_{CO_2} / n^{l}{}_{H_2O}$		= 0.001253
	$A = 0.001253/0.1131$	= 0.0111
$D = A\,[1 + (n^{v}{}_{CO_2} / n^{v}{}_{H_2O})(1 - D)]$		= 0.0123

The bicarbonate used was B.D.H. Analar which was exposed to an atmosphere of carbon dioxide in a desiccator for some weeks before use. The water and CO_2 samples were weighed to the nearest 0.1 mg on a semi-micro balance. The lowering of vapor density due to ions in solution was estimated from experimental results reported in the second paper of this series. It was

assumed in calculating values of A that the vapor density of saturated steam over the ionic solution was the same in the presence of about 10 percent (mole) of carbon dioxide, as over the solution with no other volatile present.

The experiments of Pollitzer and Strebel (1924) show that this is a safe assumption. These workers determined the concentration of water in the saturated vapor phase in the presence of various pressures of carbon dioxide. Table 3 shows approximate interpolations of their results at 50° and 70°C given as the ratio x, where x = grams of water per liter of vapor/grams water per liter of pure saturated water vapor.

TABLE 3

p_{CO_2}	5	10	20	30
x (50°)	1.10	1.15	1.35	1.6
x (70°)	1.05	1.10	1.15	1.4

The interaction of gaseous CO_2 and H_2O molecules becomes less at higher temperatures. As the pressures, p_{CO_2}, in the present experiments were usually under 5 atmospheres. it is unlikely that the assumption above introduces more than 1-2 percent error into the values of A or D.

To obtain values of K = D/P the total pressure P is required. It is assumed that $P = p'_{H_2O}[1 + (n^v_{CO_2} / n^v_{H_2O})]$ where p'_{H_2O} is the saturated water vapor pressure above the solution at the temperature, corrected for the salts in solution. The correction for dissolved carbon dioxide is small and is neglected.

In the example taken, at 257°, $p^o_{H_2O} = 44.08$ at., where $p^o_{H_2O}$ is the vapor pressure of pure water, and $p'_{H_2O} = 43.6$ at.

Therefore P = 48.5 at.,

and K = P/D = 3940 at.

This assumption is examined again below.

RESULTS

Two series of experiments were completed.

Series A.—Materials added were, 0.02 moles $NaHCO_3$, 2 cc of a solution containing 0.00797 moles HCl, and either 40 cc or 50 cc of water (20°).

Series B.—Materials added were, 0.007 moles $NaHCO_3$, 50 cc water (20°), and 5 cc of a solution containing 0.00302 moles HCl.

Tables 4 and 5 give the results obtained from Series A and B respectively.

It was found in Series B that the results obtained with the first sample of steam from a bomb filling were not so consistent as those from second or third samples taken after time was allowed for equilibrium to be re-established. This effect did not appear to be important in Series A, and no simple explanation can be offered. The results from the first samples of steam from each bomb

TABLE 4

T°C	Steam Wt. H_2O (g)	Sample Wt. CO_2 (g)	CO_2 system moles $\times 10^5$ (Uncorrected)	Vol. Soln. 20° (cc)	p'_{H_2O} (at.)	g H_2O per cc vapor $\times 100$	A $\times$ 100	D $\times$ 100	1 – D	P (at.)	K = P/D
114	0.0066	0.0347	7.38	42.75	1.59	0.0920	0.0333	0.105	0.999	5.00	4800
128	0.0091	0.0317	7.43	42.70	2.47	0.139	0.0531	0.129	0.999	6.00	4640
147	0.0186	0.0389	7.37	42.75	4.45	0.232	0.0900	0.167	0.099	8.25	4940
175	0.0335	0.0395	7.97	42.75	8.68	0.462	0.175	0.259	0.997	12.85	4960
182	0.0300	0.0277	7.37	42.76	10.21	0.531	0.219	0.301	0.997	14.1	4680
192	0.0252	0.0191	7.11	52.75	12.77	0.658	0.328	0.429	0.996	16.7	3890
195	0.0467	0.0320	6.75	52.70	13.63	0.701	0.338	0.432	0.996	17.5	4040
208	0.0182	0.0102	7.97	42.75	17.86	0.910	0.474	0.582	0.994	22.0	3770
227	0.0308	0.0131	7.45	52.75	25.65	1.30	0.628	0.737	0.993	30.1	4080
228	0.0397	0.0163	7.28	52.80	26.3	1.33	0.632	0.738	0.993	30.7	4160
228	0.0397	0.0148	7.67	42.65	26.3	1.33	0.701	0.807	0.992	30.3	3750
231	0.0479	0.0177	7.97	42.75	28.1	1.41	0.732	0.842	0.992	32.3	3840
232	0.0262	0.0097	7.97	42.75	28.3	1.43	0.711	0.818	0.992	32.6	3980
255	0.0441	0.0127	7.97	52.80	42.2	2.15	1.04	1.16	0.988	47.1	4060
257	0.0629	0.0174	7.97	52.75	43.6	2.22	1.10	1.22	0.988	48.5	3980
291	0.0954	0.0150	7.97	52.80	73.7	3.94	2.34	2.49	0.975	78.4	3150
298	0.1870	0.0249	7.97	52.80	81.5	4.36	3.03	3.19	0.968	85.9	2690
305	0.0796	0.0099	7.97	52.80	89.9	5.03	3.24	3.40	0.966	94.5	2780
314	0.1413	0.0131	7.97	52.80	101.9	5.79	5.03	5.21	0.948	105.8	2030
322	0.1658	0.0144	7.76	52.65	113.1	6.63	5.02	5.19	0.948	117.1	2250
343	0.0989	0.0068	7.97	52.80	148.1	9.75	7.9	8.1	0.919	152.3	1870
348	0.0598	0.0040	7.83	51.75	157.6	10.8	8.5	8.7	0.913	161.9	1860

TABLE 5

T°C	Steam Wt. H_2O (g)	Sample Wt. CO_2 (g)	CO_2 in system moles $\times 10^5$ (Uncorrected)	Vol. Soln. 20° (cc)	p'_{H_2O} (at.)	g H_2O per cc vapor $\times 100$	A $\times$ 100	D $\times$ 100	1 – D	P (at.)	K = P/D
163	0.0239	0.0117	2.24	55.25	6.54	0.346	0.138	0.166	0.998	7.85	4730
179	0.0485	0.0202	2.80	55.25	9.61	0.502	0.212	0.248	0.998	11.25	4530
197.5	0.0612	0.0180	2.83	55.31	13.15	0.743	0.312	0.349	0.997	14.7	4220
199	0.0454	0.0103	2.45	55.25	14.93	0.766	0.397	0.434	0.996	16.3	3760
222	0.0717	0.0121	2.81	55.25	23.62	1.20	0.647	0.692	0.993	25.2	3640
224	0.1020	0.0154	2.53	55.25	24.53	1.24	0.630	0.669	0.993	26.0	3890
227	0.1088	0.0156	2.61	55.22	25.94	1.32	0.711	0.752	0.992	27.5	3900
233	0.1048	0.0126	2.44	55.17	28.96	1.47	0.815	0.855	0.991	30.4	3550
242.5	0.1350	0.0164	2.81	55.27	34.3	1.74	0.920	0.965	0.990	36.0	3730
244	0.1112	0.0120	2.62	55.20	35.2	1.79	1.00	1.04	0.990	36.8	3530
287	0.0968	0.0060	2.85	55.20	69.8	3.72	2.11	2.16	0.978	71.6	3310
288	0.0908	0.0054	2.78	55.15	70.8	3.76	2.18	2.23	0.978	72.5	3250
317	0.1722	0.0070	2.97	55.29	105.0	6.10	4.05	4.11	0.959	106.7	2600
319	0.2264	0.0092	2.98	55.20	109.3	6.32	4.07	4.14	0.959	111.1	2680

filling in Series B are not reported. The quantity given in column 4 of the tables is the CO_2 which was present in the bomb at the time the sample was taken. This value does not include the correction for the decomposition of bicarbonate.

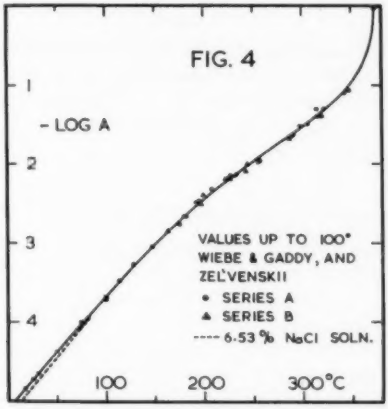

Fig. 4. Variation with temperature of the distribution coefficient A for carbon dioxide.

Figure 4 shows the values of log A at various temperatures and figure 6 the values of Henry's Law coefficient K at various temperatures. The results for A and K in Series A can be compared directly with those in Series B if it is assumed that Henry's Law is applicable. This is likely to be the case at partial pressure of CO_2 of the order of 5 atmospheres, especially as the ionization of H_2CO_3 in solution is repressed by the presence of excess HCO'_3 ions.

$$K = P/D = \frac{P}{A[1 + (n^v_{co_2}/n^v_{H_2O})(1 - D)]}$$

$$= \frac{p'_{H_2O}\ [1 + (n^v_{co_2}/n^v_{H_2O})]}{A[1 + (n^v_{co_2}/n^v_{H_2O})(1 - D)]}$$

$$= p'_{H_2O} \cdot B/A$$

$$\approx p'_{H_2O}/A$$

$B \approx 1$, as at low temperatures $(1 - D) \approx 1$, and at higher temperatures $n^v_{co_2}/n^v_{H_2O}$ becomes small compared with unity. Writing $B = 1$ does not introduce more than 0.3 percent error into any of the results. This is not significant.

p'_{H_2O} at constant temperature is an average of 0.5–.7 percent higher in Series B than in Series A because of the smaller electrolyte concentration. It cannot be expected that this will be reflected in the values of A given as it is doubtful whether they are more accurate than about $\pm$ 5 percent.

The results at temperatures from 100-200° provide a test of the assumption $P = p'_{H_2O}\ [1 + (n^v_{CO_2} / n^v_{H_2O})]$. In Series A the ratio $n^v_{CO_2} / n^v_{H_2O}$ ranges from 0.28 at 195° up to 2.15 at 114°. In Series B the ratio is 0.12 at 197° and 0.20 at 163°. If the assumption was not reasonable the values of A and K from Series A should show a definite trend away from Series B. This is not apparent.

Even if a complex of type $CO_2.nH_2O$ was formed in the vapor (Pollitzer and Strebel's results at 50° can be explained by a complex $H_2O.CO_2$) the total pressure may not be affected greatly. The total pressure, which is assumed to be the sum of $p_{CO_2} + p'_{H_2O}$, may actually be due to $p_{(CO_2.nH_2O)} + p'_{H_2O}$ where $p_{CO_2} = p_{(CO_2.nH_2O)}$.

SALTING-OUT OF GASES BY ELECTROLYTES

The solubilities of carbon dioxide reported in tables 4 and 5 are for solutions containing both $NaHCO_3$ and NaCl. The difference between the solubility of CO_2 in these solutions and that which could be expected in pure water is now examined.

The fraction of carbon dioxide ionized in a pure water solution is given approximately by

$x = (K^1_a/m.\ \gamma^2_{\pm})^{1/2}$ where K^1_a is the apparent first acid dissociation constant of carbonic acid, m the molality of the solution, and $\gamma_{\pm}$ the mean molal activity coefficient of the ions. K^1_a is not likely to rise above 7×10^{-7} (Ellis and Fyfe, 1957), m in the present experiments was not less than 0.02 moles/1000 g, and $\gamma^2_{\pm}$ at this concentration is approximately 0.96 at 25° (Harned and Owen, 1950, p. 547) and is unlikely to change by more than a few percent in liquid water at higher temperatures (Leitzke, 1955). The value of x is not likely to exceed 0.006 at the temperatures and pressures of gas used.

As the presence of excess HCO'_3 ions represses the ionization of H_2CO_3, the solubility of carbon dioxide in the bicarbonate solutions will be not less than 0.994 of the solubility in pure water (ignoring salting-out effects). This difference between unity and 0.994 is not considered further.

The solubility of a non-electrolyte in a solvent is changed by the addition of an electrolyte. The empirical Setschenow equation is often used to relate the ratio of solubility (β) at salt concentration, m, to the solubility in the pure solvent (β_0).

$$\log_{10} \frac{\beta_0}{\beta} = k.m$$

An example of the magnitude of the effect is given by the results of Morrison and Billett (1952) for the salting-out of n-butane from water solution.

The salting-out coefficient decreases with increasing temperature, and except for a few anomalous cases this behavior is general.

Electrostatic theories such as that due to Debye and McAulay (1925) consider that salting-out arises from the solution component of highest dielec-

tric constant being concentrated around the ions by their electric field, and the component of lower dielectric thereby being concentrated in the remaining solution. As the dielectric constant of water is usually higher than the solute, the latter is "salted-out" of solution.

TABLE 6

Values of k in Setschenow Eqn. (m in moles salt/1000 g H_2O)

Salt	NaCl	KCl	HCl
T°C			
12.5	0.243	0.200	0.080
30	0.217	0.182	0.049
49.5	0.194	0.164	0.031
71.5	0.176	0.144	0.028

McDevit and Long (1952) suggested that salting-out might be related to the volume change when the electrolyte is dissolved in water, or to the related "effective pressure" of the electrolyte as derived by compressibility measurements.

Neither the electrostatic theories nor the internal pressure theory are generally valid, although each can be applied with success to a limited number of systems (Morrison and Johnstone, 1955).

Salting-out is a rather complex phenomenon. It depends on the size of the added ions, their charge, the nature of the non-electrolyte, the salt concentration, and the temperature. The simple theories mentioned do not take into account specific interaction between ions, solute molecules and solvent molecules.

Although there is no satisfactory detailed quantitative theory to predict the change in salting-out with temperatures much above room temperatures, qualitatively it can be predicted to decrease. The effect is related to the solvation of the ions and solute molecules in solution, and to changes in the structure of water in the presence of ions (Frank and Evans, 1945). The average number of water molecules associated with the solvation sheath about an ion decreases with increasing temperature, while at the same time water tends to a random arrangement of molecules.

The solubility of CO_2 in a 6.53 percent solution of sodium chloride is given by Seidell (1940). The values of the Bunsen coefficient β and the coefficient A are given in table 7 for pure water and the salt solution.

The figures are probably not of great accuracy but they show the marked decrease in salting-out between 0 and 60°. From these figures it appears that at 100° the ratio of solubility in water to that in a 4-5 percent salt solution is about 1.05. The trend of solubility in a 6.53 percent NaCl solution is shown with the present results in figure 4.

The solubilities reported for Series A are possibly 5 percent low about 100°, but over about 150° it can be anticipated that the solubilities will equal those in pure water within the reproducibility of the present experiments. The

TABLE 7

T°C	β_0	β 6.53% NaCl	$A_0 \times 10^5$	$A_{(6.53\ NaCl)} \times 10^5$	Ratio $\frac{A\ (water)}{A\ (NaCl\ soln.)}$
0	1.713	1.234	0.835	0.614	1.36
10	1.194	0.875	1.17	0.877	1.33
20	0.878	0.664	1.64	1.27	1.29
30	0.665	0.517	2.26	1.79	1.26
40	0.530	0.414	3.14	2.51	1.25
50	0.436	0.370	4.34	3.76	1.15
60	0.359	0.305	5.81	5.04	1.15

solubilities from Series B can be taken as equal to solubilities in water within the significance of the results.

DISCUSSION OF CARBON DIOXIDE SOLUBILITY

The solution of gases in water compared with solution in organic solvents is unusual in many respects.

The temperature coefficients of gas solubility in water are negative at low temperatures, and the rate of change of solubility with temperature is very high, i.e. the partial molal heat capacity $\bar{C}_p$ of the gases in solution is very large. Eley (1939, 1944), and Frank and Evans (1945) pointed out that at room temperatures the entropy change, ΔS_s, associated with the solution of a given gas is 10-12 e.u. more negative for water than for organic solvents. At room temperatures the partial molal volume of the dissolved gas is smaller in water than in organic solvents.

It is convenient to consider the energy of solution of a gas in a liquid as the sum of two terms (Eley, 1939, 1944).

$$\Delta E_s = \Delta E_C + \Delta E_A$$

ΔE_C is the energy of creating a cavity of a sufficient size in the liquid to contain the gas molecule, and ΔE_A is the energy associated with placing the gas molecule in the cavity. ΔS_s can be divided in the same manner.

$$\Delta S_s = \Delta S_C + \Delta S_A$$

Eley showed that ΔE_A and ΔS_A for the solution of an inert gas do not differ greatly for organic solvents and water. The differences between solvents arise mainly from the terms ΔE_C and ΔS_C. At low temperatures in water Eley concluded that ΔE_C was very small, and that solution of gas occurred into interstitial positions in the open structure of water. This would also explain the low values of the partial molal volume, $\bar{V}$, for gases in water.

$\Delta E_C = T.\ \bar{V}.\ \alpha/\beta$, where α is the thermal expansion coefficient of the solvent, and β its compressibility. The rapid increase in α with temperature causes a similar increase in ΔE_C.

At low temperatures in water $\Delta E_C < -\Delta E_A$ and the temperature coefficient of solubility in the liquid is negative. With increasing temperature, as ΔE_C becomes equal to and then greater than $-\Delta E_A$, the temperature coefficient passes through zero and then becomes positive.

In organic liquids and high temperature water a dissolved gas molecule occupies one of the quasi-lattice sites in the close-packed structures. The energy ΔE_C of forming a cavity on this site is greater than $-\Delta E_A$ and therefore the temperature coefficient of solubility is positive (Eley, 1939).

There is a loss of entropy through the confinement of a gas molecule when it is dissolved in the solvent. There may be also a breaking-down of the solvent structure with a consequent gain in entropy. This is significant mainly in solvents with a close-packed structure. The large loss of entropy and the negative values of ΔH_s associated with the solution of inert gases in water at room temperatures was explained by Frank and Evans (1945) by the structure of water being modified towards greater crystallinity. They suggested that each gas molecule is surrounded by an "iceberg" or region of definite solvent structure.

In the vapor and liquid phases the chemical potential (μ_a) of a gas (a) is given by

$$\mu^v_a = \mu^\dagger_a\,(T) + RT \ln f_a \quad \text{and}$$
$$\mu^1_a = \mu^\bullet_a\,(T) + RT \ln x_a.\gamma_a$$

where $\mu^\dagger_a$ and $\mu^\bullet_a$ are the chemical potentials in the standard states of unit fugacity in the vapor phase and a hypothetical mole fraction of unity in the solution, f_a is the fugacity of the gas, and x_a and γ_a the mole fraction and activity coefficient of the gas molecules in solution.

At constant temperature for the solution process

$$a(\text{vapor}) \rightarrow a(\text{solution})$$

at equilibrium, $\Delta G = O = \mu^1_a - \mu^v_a$

$$= \mu^\bullet_a - \mu^\dagger_a + RT \ln \frac{x_a\ \gamma_a}{f_a}$$

$$= \Delta G^0_s + RT \ln \frac{x_a\ \gamma_a}{p_a\ \alpha_a}$$

(α is the fugacity coefficient of the gas).

Where Henry's Law is obeyed $\gamma_a/\alpha_a = 1$, and $\Delta G^0_s = -RT \ln \frac{x_a}{p_a} = RT \ln K$

Figure 5 shows the relationship of RT ln K to temperature. ΔS^0_s was obtained from graphical differentiation of this type of plot, and ΔH^0_s from the equation

$$\Delta H^0_s = \Delta G^0_s + T\Delta S^0_s$$

The values of these three thermodynamic functions are given in table 8. The bracketed values are those given by Frank and Evans (1945). The values are intended mainly as an illustration, and at higher temperatures can be regarded as only semi-quantitative.

The change in heat and entropy associated with the vaporization of gas from solution decreases as the temperature rises. This can be correlated with the change in water structure from an open tetrahedral arrangement of molecules at low temperatures to a close-packed liquid at high temperatures.

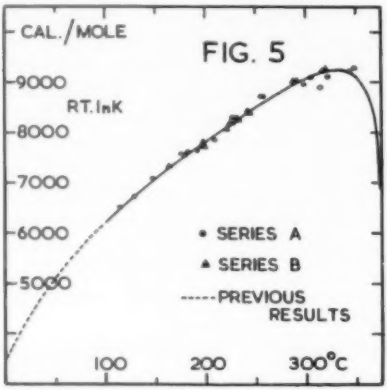

Fig. 5. Graph of the free energy of solution of carbon dioxide versus temperature.

TABLE 8

T°C	25	40	100	150	200	250	300
ΔG°_s (cals.)	4380	4840	6270	7130	7880	8500	9030
$-\Delta S^\circ_s$ (e.u.)	31.5 (30.6)	28.5 (28.2)	20.5	16.0	13.5	12	8
ΔH°_s (cals.)	-5010 (-4730)	-4090 (-3870)	-1380	370	1490	2200	4400

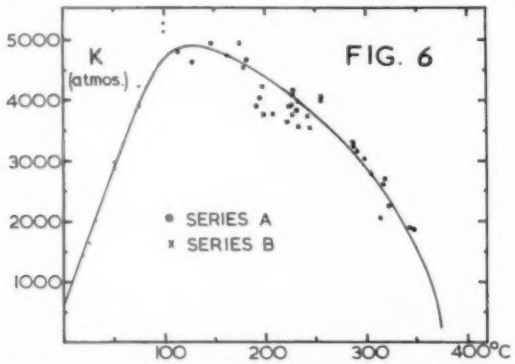

Fig. 6. The variation with temperature of the solubility of carbon dioxide represented by the Henry's Law coefficient, K. The results up to 100° are from Wiebe and Gaddy, and Zel'renskii.

About 200°, ΔS for vaporization of carbon dioxide from solution becomes approximately equal to that for vaporization of an inert gas from an organic solvent at room temperatures. For the latter process ΔS is not expected to vary greatly with temperature (Eley, 1939).

Table 9 gives for comparison the values of ΔS°_s for solution of helium and water in methyl alcohol-water mixtures (Law, 1949). The change in

ΔS°_s with increasing methyl alcohol content is similar to the effect of increasing temperature for pure water solutions. In both cases there is a collapse of the open structure of low temperature water.

TABLE 9

Entropy of Solution at 25° for Helium and Argon in MeOH—Water Mixtures

Mole % MeOH	0	20	40	60	80	100
$-\Delta S^\circ_s$ (Argon)	29.4	23.2	19.3	18.0	17.2	16.6
$-\Delta S^\circ_s$ (Helium)	25.1	21.0	17.7	16.2	14.8	13.9

For the carbon dioxide solutions ΔG°_s reaches a maximum at about 340°C and ΔS°_s becomes zero. At higher temperatures ΔS°_s becomes increasingly positive, reaching a high value at the critical point. Near to the critical point, insertion of gas molecules into the liquid further weakens the already weak water-water adhesive forces and ultimately causes the liquid phase to become unstable with respect to a supercritical fluid. A large positive entropy change is associated with this process.

APPLICATION OF RESULTS

The present results, while not of high precision, are the only high-temperature solubility values available for carbon dioxide. They demonstrate the general solubility behavior of gases in water at high temperatures.

The principles involved in calculating conditions of equilibrium in systems containing carbon dioxide and metal carbonates have been adequately discussed by Garrels and Dreyer (1952). The methods of calculation can be used at any temperature. It is sufficient in this paper to point out the fallacy of extrapolating results from low-temperature gas solubility experiments by assuming a continuous decrease in solubility with increasing temperature. This procedure has been used in several geological and mineralogical papers. The partial pressure of a gas above a given solution does not increase continuously with temperature, but after passing through a maximum value, approaches a pressure determined by the mole fraction of the gas and the total pressure in the system.

The information summarized in figure 1 is useful in interpreting processes of liquid-vapor separation that occur in natural hydrothermal systems. At high temperatures, carbon dioxide and ammonia remain more soluble than gases such as hydrogen, oxygen, nitrogen and the rare gases, but the distribution behavior of small quantities of all gases tends to become equivalent near the critical point of water.

Information on the temperature of separation of liquid and vapor phases in hydrothermal systems can be obtained by utilizing the ratios of the more soluble gases, ammonia and carbon dioxide, to the less soluble gases such as nitrogen or hydrogen contained in the gas of the steam from fumaroles, hot-springs or drill-holes, e.g., Wilson (1955).

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DISCUSSION

ON THE PERMIAN CLIMATIC ZONATION AND PALEOMAGNETISM

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Palaeomagnetic measurements have been interpreted as demonstrating that the positions of the continents have moved relative to one another and to the axis of rotation through geological time (Creer, Irving and Runcorn, 1954; 1957). The former inference has been drawn because the positions of the mean magnetic pole calculated from rocks of the same age from different continents are not in agreement. The latter inference is true if on the average the geomagnetic axis and the earth's axis of rotation coincide. This hypothesis is firmly based on theoretical grounds (Creer, Irving and Runcorn, 1957, and Runcorn, 1959). Evidence for this hypothesis is provided by the fact that the mean geomagnetic axis in late Tertiary times coincides with the present position of the geographical axis. In the ultimate analysis however the test of this hypothesis is to determine whether the results of paleoclimatic studies are consistent with the results of paleomagnetic studies. The use of paleontological evidence to this end is based on the recognition that, although there may in the geological past have been variation in the mean climate of the earth, a zonation in the distribution of fossils roughly symmetrical about the axis of rotation would still be expected. Thus for any geological period, provided that the continents are placed in the positions relative to one another and to the axis of rotation which they occupied at that time, the observed occurrence of fossils in the rocks of that age should show this zonation.

Recently, Stehli (1957) has examined the zoogeographic patterns in Permian times assuming that the present distribution of the continents and the present position of the geographical axis prevailed. He states that of the Permian marine invertebrates many appear to occur randomly, but that some groups of brachiopods and fusulinids appear to have a northern range lying between the present 50° and 60° N latitude. He concludes that this boundary indicates the position of the boundary between the temperate and subtropic water of Permian times. He further concludes that

> The inference from these data that the poles occupied approximately their present positions in the Permian is in complete disagreement with the interpretation of remanent magnetism data by Runcorn (1956a) who suggests that the Permian north pole was in a position within what is here believed to have been the tropical and subtropical temperature belt of Permian time.

and further

> The faunal boundary parallels the earth's present equator and, if truly caused by temperature, precludes the possibility of changes in the positions of the poles with respect to the major land masses of the northern hemisphere . . . . The data are not in accord with data derived from remanent magnetism of rocks.

In view of Dr. Stehli's statements it is surprising that his paper does not include a comparison of the paleontological data with the paleomagnetic data. It is the purpose of this note to show that the distribution of the fusulinid and brachiopod groups fit the predictions of palaeomagnetic data slightly better than they fit the present distribution of the continents; the paleontological

data is not decisive on the point but provides no justification for Dr. Stehli's conclusion.

Study of the figures in his paper shows that not only are these fossil groups almost entirely absent from the 21 major outcrops of Permian marine rocks north of the present 55°N latitude line, but they are also largely absent in the (fewer) outcrops south of the present equator. The table (below) derived from his figures 2, 3 and 4, shows this to be true. But the principle of zonation suggests that not only is a certain fossil group likely to occur with greatest frequency between certain latitudes but that the distribution pattern is likely to be symmetrical about the equator of that geological time.

The positions of the equators and poles for the Carboniferous, Permian and Triassic periods calculated from rocks from Great Britain have been given by Creer, Irving and Runcorn (1954, 1957) and from rocks from North America by Runcorn (1956a). In Triassic times and earlier there is evidence, (Runcorn, 1956b) that these continents were roughly 24° closer to each other than they are at present. Figure 1 shows the position of these equators and poles on a sterographic projection of the northern hemisphere, adjusted to allow for this continental drift. Comparison with figures 2, 3, 4 and 5 of

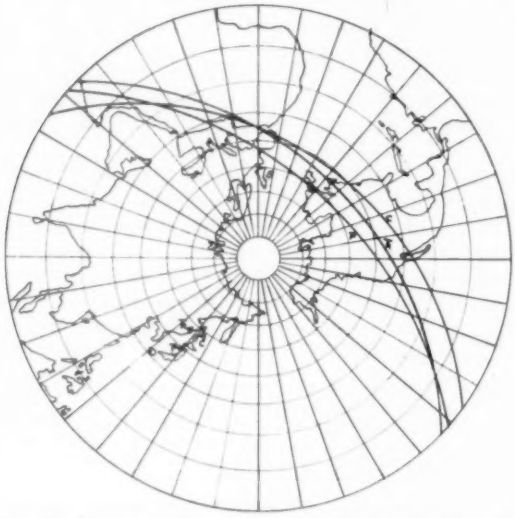

Fig. 1. Position of poles and equators for Carboniferous, Permian, and Triassic times from paleomagnetic data from Britain and North America.

Stehli's paper shows that the brachiopod and fusulinid groups, which he considers to have been subtropical, occur with roughly equal frequency on either side of the equator in Europe and North America.

It seems therefore that the positions of these continents in Permian time, given by paleomagnetic evidene, fit Stehli's data better than the present dis-

tribution of the continents.

An apparent discrepency is the relative abundance of these fossils in Asia near the position of the Permian pole plotted on the present map of the world on the basis of the North American and European paleomagnetic results. But it was pointed out by writers on paleomagnetism (Runcorn, 1956c, and Irving, 1956) that, as the paleomagnetic evidence suggested that continental drift as well as polar wandering had occurred, the position of the continent relative to the pole could not be determined from paleomagnetic observation made in other continents. Thus the present distribution of the continents is not the suitable basis on which to consider paleoclimatic data: instead the paleomagnetic and paleoclimatic data for each landmass must be separately compared. In fact, of course, there is evidence to suggest that India has moved north relative to Europe since the Mesozoic (Irving, 1956; Clegg, Deutsch, and Griffiths, 1956). We have as yet no paleomagnetic observations from the rest of Asia and hence no evidence concerning its possible motion in respect to Europe. But the abundance of evaporites and dune sandstones of the early Mesozoic and late Paleozoic in Northern China hardly suggests that this part of Asia had a position close to the North Pole at that time. The abundance of warm water invertebrates is in agreement with this surmise. That Asia could have moved relative to Europe appears not to have been discussed previously but its possibility must be entertained in continental drift theories.

Table Showing Numbers of Major Outcrops of Permian Marine Rocks Between Certain Circles of Latitude on the Present Globe

	Major outcrops of Permian marine rocks	Outcrops showing absence of both Richthofinid and Oldhaminid brachiopods (Stehli fig. 2)	Outcrops showing absence of brachiopod sub-family Enteltinae (Stehli fig. 3)	Outcrops showing absence of various fusulinid groups (Stehli fig. 4)	Outcrops showing absence of various brachiopod groups (Stehli fig. 5)	Mean percentage of outcrops showing absence of brachiopods and fusulinids
North of 55° N	21	20	20	20	20	95
between tropic of Cancer and 55° N	37	18	17	17	25	50
between equator and tropic of Cancer	5	2	1	1	4	40
between equator and tropic of Capricorn	8	6	5	5	6	70
south of tropic of Capricorn	9	9	9	8	9	95

The absence of these fossils from the continents of South America, South Africa, India and Australia is in good agreement with the positions close to the pole assigned to these continents by palaeomagnetic measurements on late Paleozoic rocks in Australia by Irving and Green (1958), in South Africa by Nairn (Creer, Irving, Nairn and Runcorn, 1958) and, of course, by the evidence of the great Permo-Carboniferous glaciations.

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REPLY

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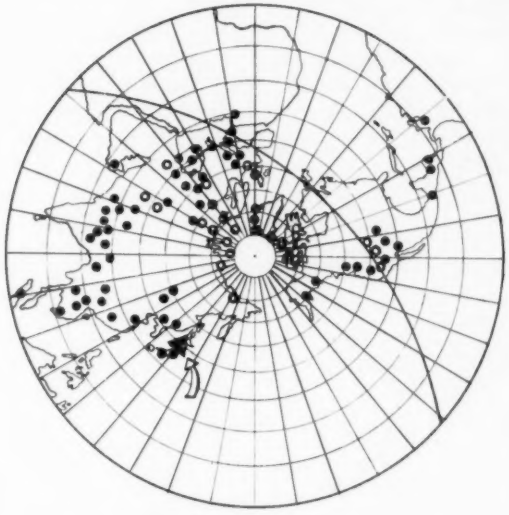
Runcorn points out in the opening sentence of his discussion of Permian climatic zonation and paleomagnetism, that one can interpret paleomagnetic measurements "as demonstrating that the positions of the continents have moved relative to one another and to the axis of rotation through geological time." If it is possible not only to drift the continents but also to shift the axis of rotation, the resulting system is one of great latitude, hence almost any set of data can be satisfied by one continental and/or axial configuration or another. For instance, on the evidence of paleomagnetic measurements from the northern hemisphere, Runcorn places the Permian north pole in Japan. On the basis of similar measurements made in Australia, Irving and Green (1958) place the Permian pole in northwestern Africa or in Spain. This divergence in results is cited as evidence that Australia has undergone relative continental drift at least sufficient to explain the variation in results. An alternative explanation may be presented, however, which should be considered: this is the possibility that paleomagnetic data are either unreliable or not being properly interpreted.

Because paleomagnetic measurements can be used to support almost any continental configuration it is difficult to see how they can be of more than limited value until consistent results can be obtained from different areas or


● OCCURRENCE OF WARM WATER INVERTEBRATES
o NON-OCCURRENCE OF WARM WATER INVERTEBRATES
▲ PERMIAN NORTH POLE
— PERMIAN EQUATOR

until a sufficient body of results is available to show that all of the data for a given geologic time support a single model. For the present, light can be shed on the validity of the method only by comparing its results with those of independent lines of evidence indicating continental configurations.

Accordingly, I presented some paleogeographic data which appeared to me to indicate that no major change in continental configurations was required since Permian time. Runcorn in his discussion has stated that these data better fit an earth model based on paleomagnetic measurements than the present-day earth model, which I employed. In figure 1 of the present note a composite of the paleozoographic data has been superimposed on Runcorn's map. It is difficult for me to see the basis for Runcorn's conclusions that the data fit his paleomagnetic earth model. What Runcorn has termed "an apparent discrepancy" in Asia appears to me, if one were to use northern hemisphere data alone, to suggest a Permian equator at a high angle to that proposed by Runcorn as best fitting the data.

Runcorn provides a table indicating the percentages of outcrops within certain limits of latitude which lack the fossils interpreted as indicating warm water conditions. This table is based on a model of the earth with the present continental configuration. He does not provide a comparable table based on his paleomagnetic earth model and in view of the poor fit of his model to the data in the northern hemisphere as shown in figure 1, it is not clear to me how Runcorn arrives at the conclusion that the data better fit his paleomagnetic than a present-earth model.

I have previously indicated some of the difficulties encountered in the interpretation of paleozoographic data. It should be stressed that my conclusions are interpretations and that interpretations can and often must be changed with the discovery of new data. At present, however, the interpretation previously presented still seems the most reasonable that can be drawn from the available data.

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Fig. 1. Composite of paleozoogeographic data plotted on Runcorn's model of the Permian Earth.

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